SELECTIVE FLOCCULATION OF COAL AND SHALE

by

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ABSTRACT

The work presented within this thesis describes an investigation into the selective flocculation behaviour of coal/shale slurries using commercially available polyacrylamide polymers. It is considered that selective flocculation may eventually offer a method of recovering the valuable combustibles which are presently discarded. To date, although numerous, mainly laboratory scale, investigations using organic polymers have been conducted on a variety of mineral combinations, little work has been undertaken on coal/shale slurries.

Selective flocculation depends essentially on differences in the adsorption of a flocculant on different minerals, which in turn depends on the comparative mineral surface chemistry. The effective dispersion of one component is also essential i.e. it must form a relatively stable suspension, either inherently or after modification with a suitable reagent. The effect of these two factors on both single specie flocculation and selective flocculation is discussed in some detail. Testwork was conducted throughout using pure coal and shale samples in order to minimise any natural variation in surface properties which may occur.

In order to define possible conditions under which a separation may be feasible, the flocculating ability of various types of polyacrylamides on separate coal and shale slurries was initially established. However, the predictions were not entirely successful with the results indicating that, in a 50/50 w/w mixed slurry, under approximately neutral conditions, coal was the preferentially

flocculated component. This was apparent for polymers of various molecular weights and ionic characters.

Variations in the surface chemistry of the coal and shale may be influenced by several factors such as pH, dispersant concentration and promoter effects. Solids concentration is another important physical aspect. Each of these were studied and discussed. Zeta potentials of the individual coal and shale samples at various pH levels were also determined and related to the selectivity and efficiency of separation under similar conditions.

It was apparent that although coal was preferentially flocculated, the major problem was that of entrainment. This inevitably arises during the formation of the coal flocs, trapping some unwanted, and essentially dispersed, shale. In addition polyacrylamide may possess a weak affinity for the shale surface. These two mechanisms lead to products with a minimum ash content of between 31 - 36%. It was also found that the flocs formed were so weak that they ruptured even on gentle agitation - hence trapped material could not be released. The effect of pre-conditioning the coal surface prior to flocculant addition was also assessed and achieved some degree of success, but again products of below 30% ash were not possible.

It was therefore concluded that while coal may be selectively flocculated from a coal/shale slurry, using commercial polyacrylamide polymers, without an additional cleaning stage(s) the system is not economically viable.

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CHAPTER 1

INTRODUCTION - THE PROBLEM OF COAL FINES

The major role of coal in both the near and medium term is felt to be in the industrial and power generation markets, both to replace oil and to meet increasing demand. In 1980 the total U.K. energy requirement was 313 Mt/a*, of which 121 Mt/a was coal (1) Since coal reserves are large (245 years) in comparison with other fossil fuels (≃ 35-60 years), it is expected to play an important role as a future energy source (2) and as a feed stock for the chemical industry.

A typical flowsheet for a modern coal preparation plant is depicted in Fig. 1.1. Basically it consists of two sections; one for the treatment of coarse coal, that is above 500 μm, and one for fine material below this size. Coarse coal separation processes make use of the differences in densities between coal (1.3) and shale (2.6). Jigging and dense medium separation are well established and have remained virtually unchanged in fifteen years (3) These gravity methods however are not practical for particles finer than 500 μm and other methods must therefore be found.

In the past thirty years, due to increased mechanisation in coal winning, the percentage of -500 μm material, as a proportion of ROM, has increased from 10% to 20% (4). Compounding this problem are the facts that the percentage of superfine (- 63 μm) material in this fraction is ≃ 60%, and that its ash content is also increasing. The

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* million tonnes of coal equivalent

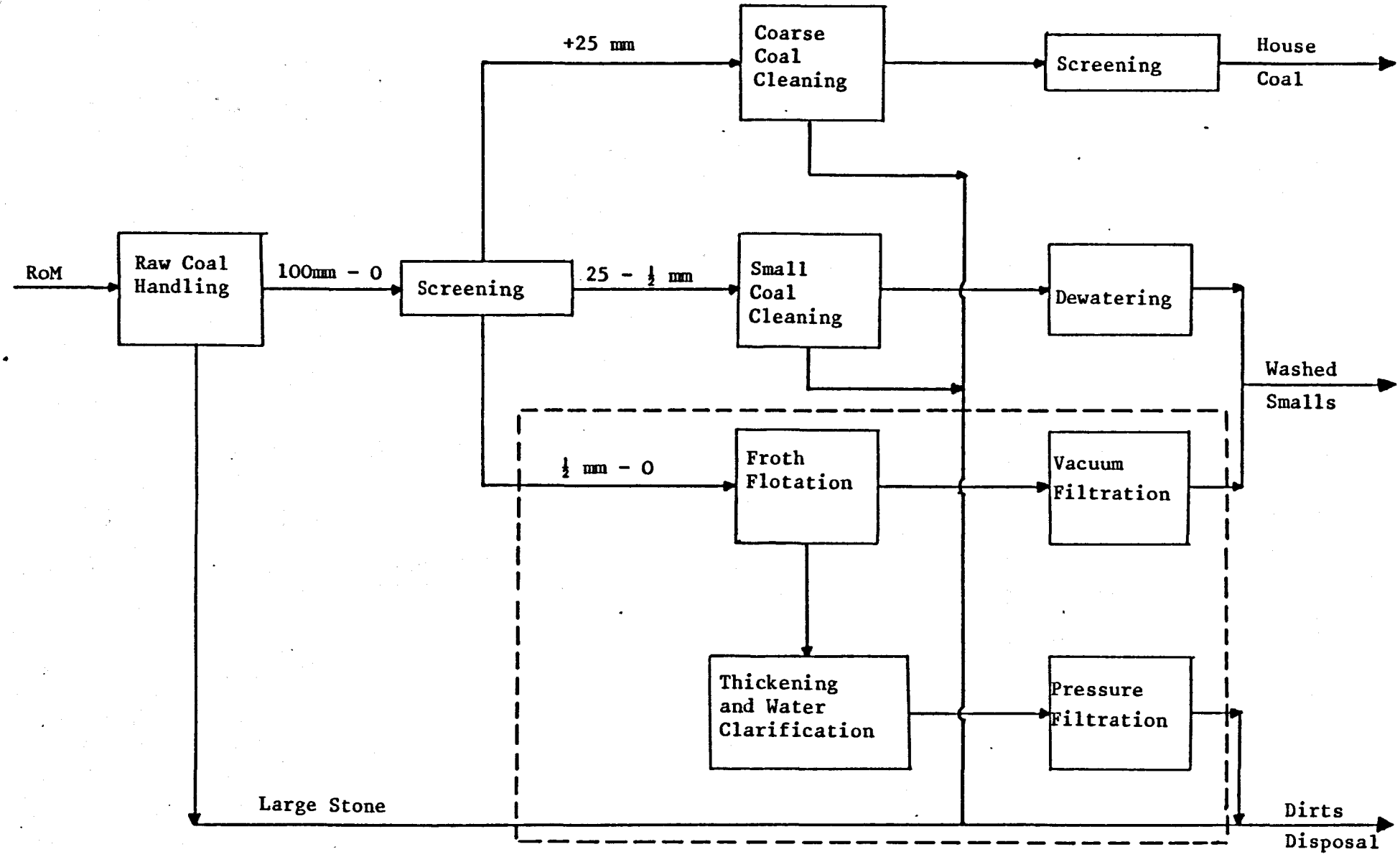


Figure 1.1 Flowsheet for Coal Preparation Plant

problems of fine coal treatment are extensive and the cost of treatment high. This is an important factor to consider in the treatment of such a relatively low value mineral as coal. In fact preparation costs of the 20% of fines are estimated at more than 2½ times those of the other 80% of the mineral (4).

A breakdown of the current markets for coal is given in Table 1.1. From this it can be seen that some 80% of saleable coal, and, more importantly, all of the fine coal, is sold for power generation and the coking coal markets, hence it is these areas which are most affected by fines content.

Table 1.1 Markets for Coal in 1980-81 (5)

Market	Demand Mt/a
Electricity	87.8
Coking ovens	11.3
Low Temperature carbonisation plants	2.9
Industry	7.4
Domestic	8.5
Transport	0.1
Public Administration/Misc.	1.7
Collieries	0.6
TOTAL	120.3

Temporary solutions to the fines problem were first achieved by blending untreated fines into the coarser washed product; with resultant filtration and handleability difficulties. The use of froth flotation, to produce a cleaner fines product, has helped to partially alleviate some of the difficulties. However, the presence

of ultrafine clays produces slimes coating on the coal, reducing reagent adsorption and increasing coal losses to the tailings. Entrainment of clays in the froth also occurs, leading to a higher ash product, with poor filtration properties and high residual moisture contents. The increase in final smalls moisture, from 9.3% in the 50's to 12.4% today, is not particularly damaging at present, but any further increases could lead to extreme handleability problems (see Fig. 1.2).

Ideally it would be beneficial to remove slimes prior to flotation, leading to reduced reagent additions and a cleaner, drier, more easily filtered product. However, discarding the slimes may result in the loss of valuable combustible material. A method of processing ultrafine material for the recovery of valuable combustibles is therefore necessary. Selective flocculation would appear to offer a viable method of achieving this, offering obvious cost advantages over other proposed methods such as spherical agglomeration (6).

Selective flocculation is the flocculation of one mineral species from a mixture, thus allowing a separation based on differential settling rates. To date its development has been limited mainly to laboratory studies and as such may be considered to be at a stage similar to that of the early evolution of the flotation process. However, the experience gained in flotation is now available for use in the development of reagents for selective flocculation. In the following chapters this experience is utilised to the full.

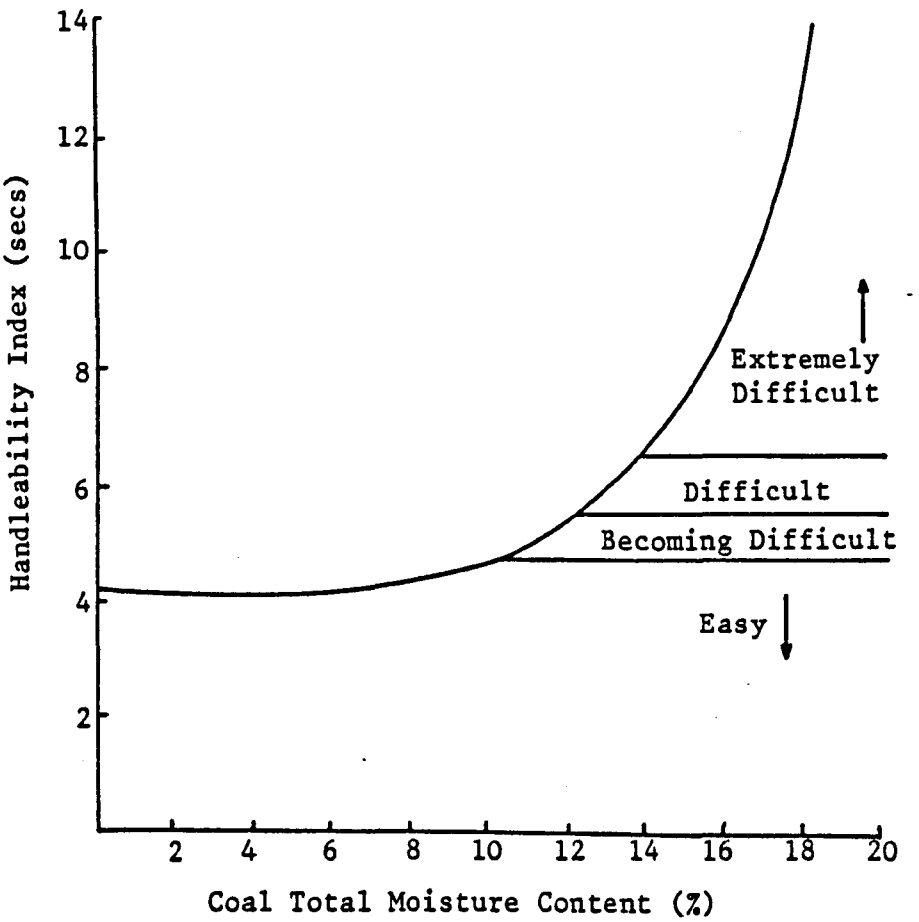


Figure 1.2 Handleability Curve - Small Coal (25 mm - 0)

CHAPTER 2

FUNDAMENTALS OF PARTICLE AGGLOMERATION

This chapter is a review of the mechanisms concerned with the basic theory of particle agglomeration and stabilisation. This is necessary in order to facilitate a fuller understanding of the processes involved. It includes a literature survey of polymer adsorption at mineral surfaces and the reported work on selective flocculation.

2.1 PARTICLE STABILISING MECHANISMS

The stability of any dispersed system is dependent upon several factors including the potential energy which exists between solid particles as they approach each other. This potential energy can be considered to be the resultant of two forces; attraction and repulsion, the former being due to London-Van der Waals forces and the latter due to any residual charge on the particles. Figure 2.1 illustrates this.

The summation of these two forces represents the actual potential energy curve followed by two particles approaching each other. The inherent stability of a two-phase system is determined by the height of the maximum value on the curve. If the maximum is low then particles will tend to coagulate and settle out, but if the maximum is high then a stable dispersed state will probably result. Two methods are available to overcome the maximum in the potential energy curve:

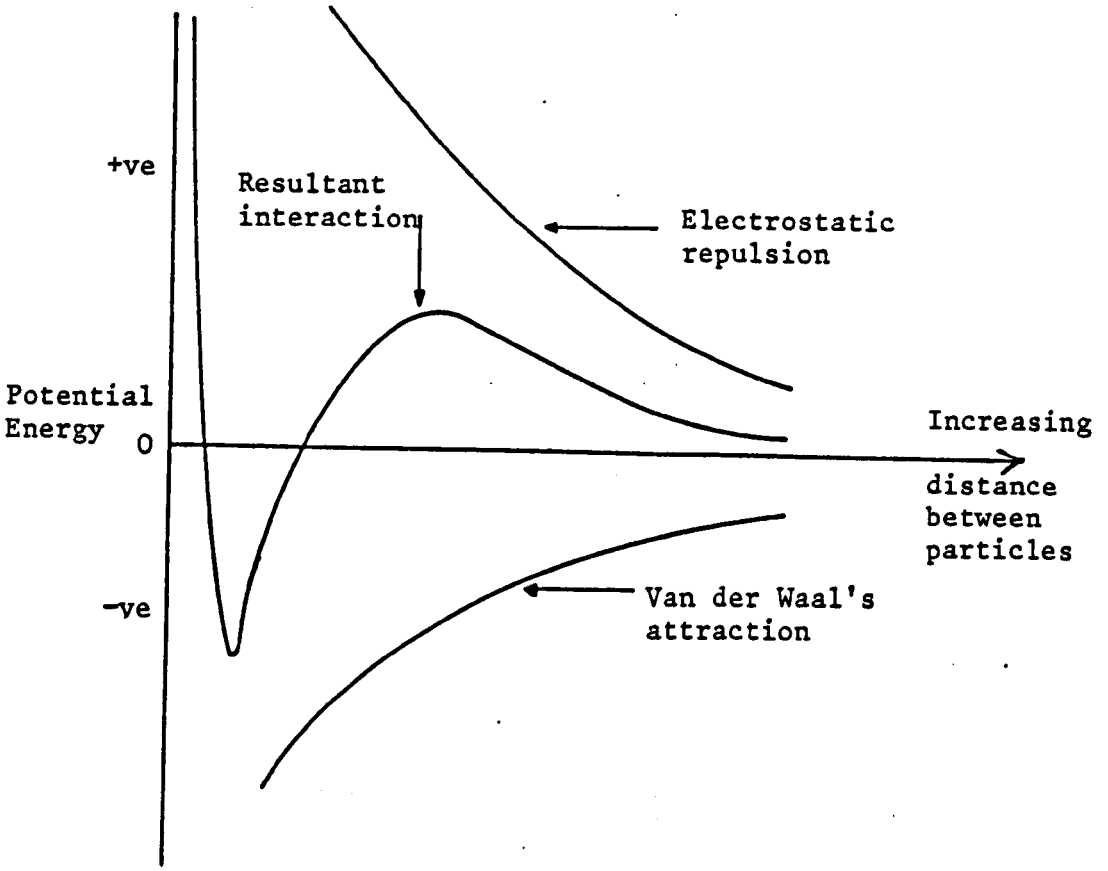


Figure 2.1 Potential Energy Curve

2.1.1 Coagulation

Coagulation usually occurs with the addition of inorganic multivalent electrolytes, such as calcium or ferric chloride, which reduce the repulsive forces between electrocratic colloids. This allows them to agglomerate via van der Waals forces and may occur in two ways:

i) Double layer repression - the double layer thickness is reduced on increasing counter ion concentration, as seen in Fig. 2.2 The quantity of surface charge is not reduced greatly but the extent to which its influence extends from the surface is decreased. Shaw (7) has calculated, theoretically from the Derjaguin, Landau,

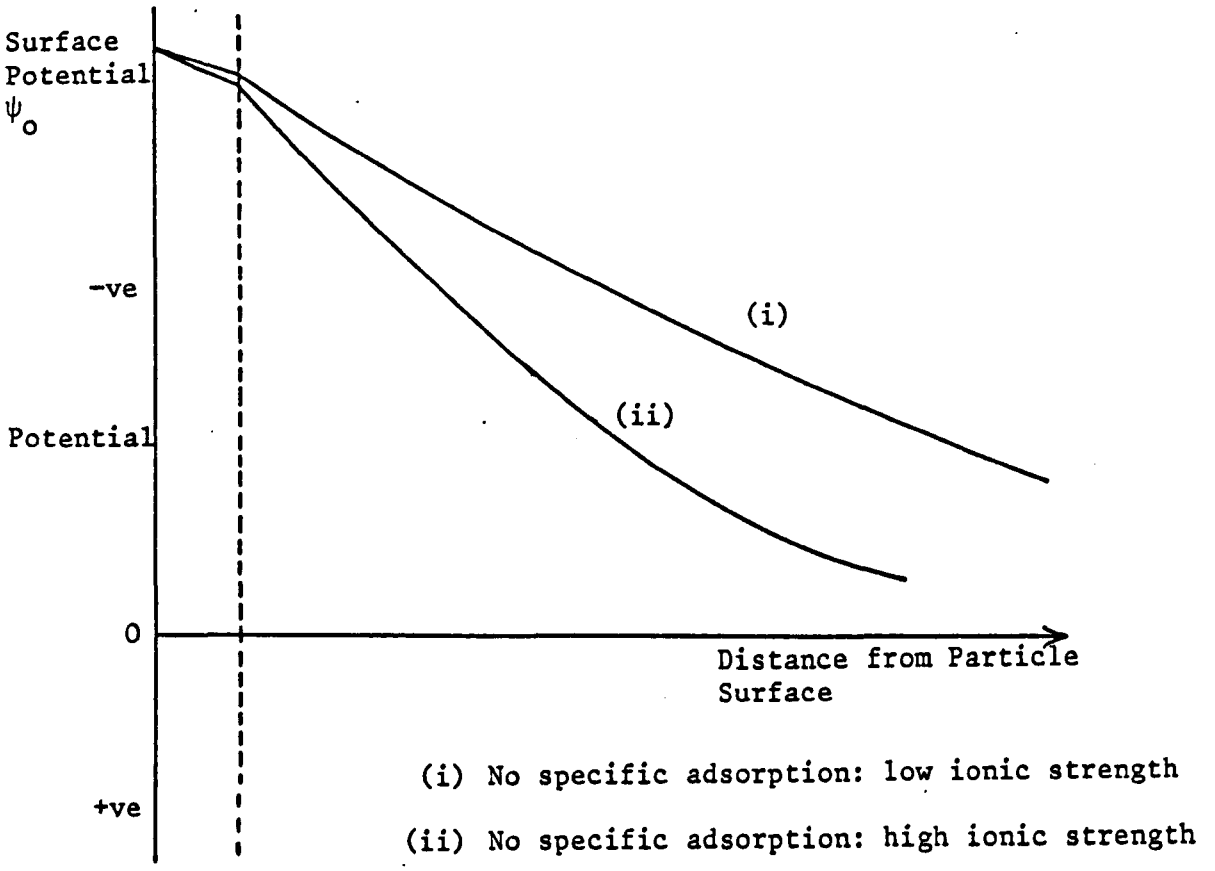


Figure 2.2 Double Layer Repression (8a)

Verwey, Overbeek theory (DVLO), that the coagulating effect increases markedly with the valency of the counter ion.

ii) Adsorption coagulation - counter ions which specifically adsorb in the Stern layer, interacting directly with the particle surface, bring about a reduction in surface energy, creating coagulation as illustrated over in Fig. 2.3.

It is possible, however as shown by (ii), to restabilise this system by the addition of excess coagulant, which may reverse the charge on the particle.

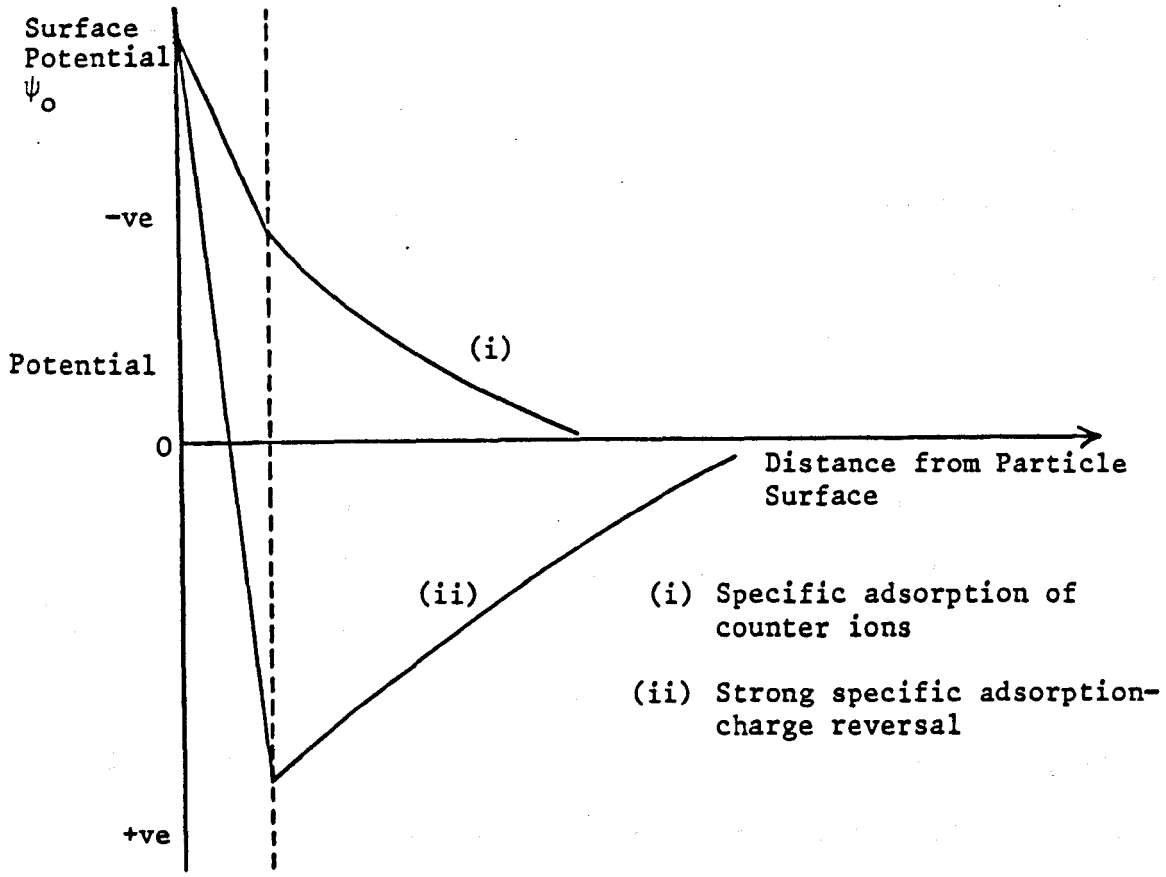


Figure 2.3 Adsorption Coagulation (8a)

2.1.2 Flocculation

Following La Mer's plea (9) the term flocculation is used to describe destabilisation of particles by the addition of long chain polymers. Particles bonded in this way form flocs of a much larger size and consequently are able to settle out of a suspending liquid more readily.

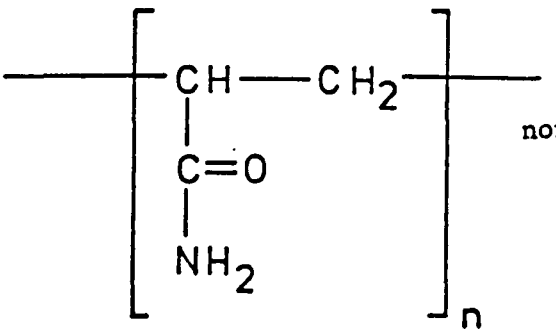
2.1.2.1 Definition of flocculation and its use in the mineral processing industry

Flocculation, as currently used in the mineral industry, may be defined as the aggregation of finely divided particles by the addition of organic, water soluble, long chain polymers of high molecular weight.

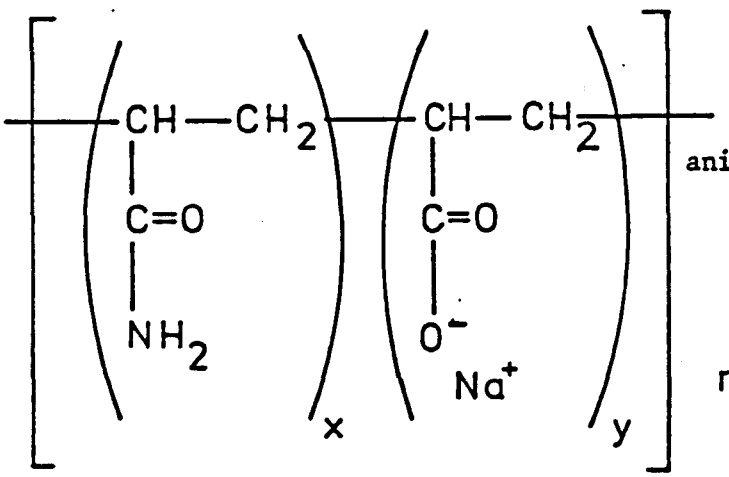
Natural flocculants such as guar gum, starch and dextrin, are generally of lower molecular weight, than synthetic flocculants, are less effective and require large dosages. However, guar gum is still in extensive use in the uranium industry.

Synthetic flocculants, introduced in the 1950's, have become increasingly popular, despite their higher cost. Of the synthetic flocculants available, polyacrylamide and its derivatives are the most commonly encountered. Their molecular weights can vary from $0.5 - 23 \times 10^6$ and since the molecular weight of the monomer is 71, a flocculant of molecular weight 14×10^6 would contain 197,183 repeating units, i.e. a degree of polymerisation of 197,183. Also, since the length of a carbon to carbon bond is 1.54×10^{-10} m, the polymer chain, if fully extended, would be 30 μm long! However, the polymer chain is coiled considerably in solution (see section 1.3.1.4) and hence the molecule size in any one dimension would be much less than this (8b). Polyacrylamide itself is non-ionic; co-polymerisation of acrylamide-acrylic acid, or partial hydrolysation of polyacrylamide introduces anionic character, whilst the cationic derivatives are prepared by co-polymerisation of acrylamide with tertiary amine or quaternary ammonium compounds. The structures of these are shown over. The lowest molecular weights are found with the cationic derivatives; these are also the most difficult to produce and hence the most expensive.

Since a necessary consequence of the wet processing methods practised in many engineering industries is that at one or more stages in the process the solid phase must be separated from the liquid phase, synthetic polymeric flocculants have been in use in

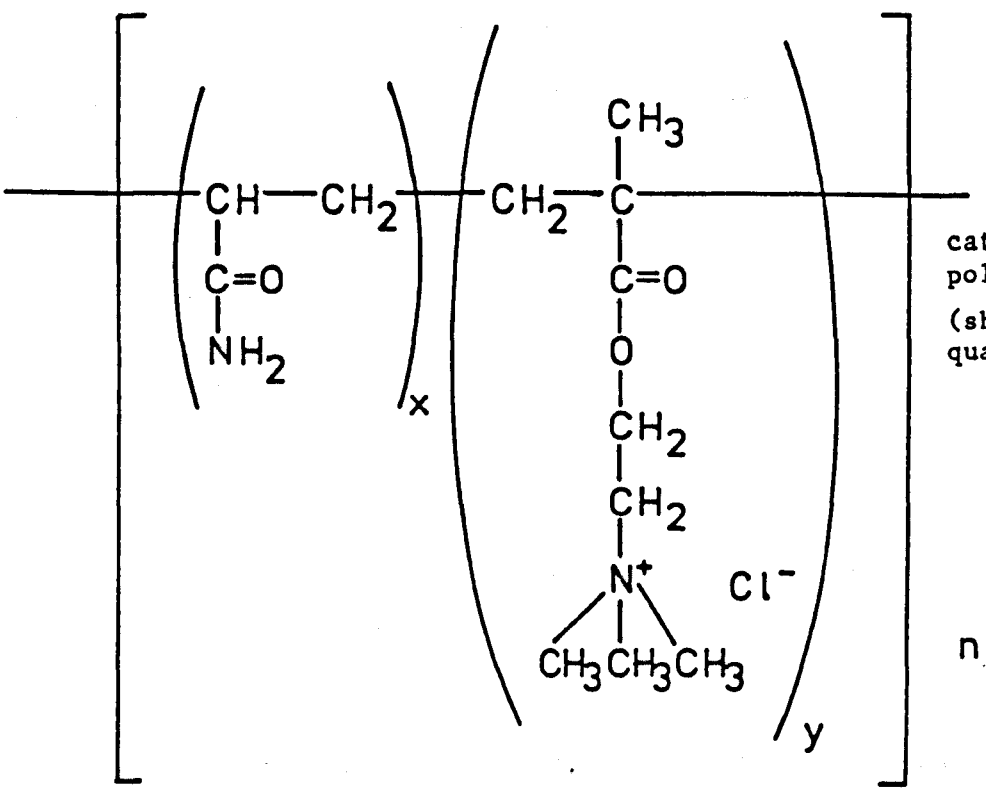


non-ionic polyacrylamide



anionic polyacrylamide

$n = x + y$



cationic polyacrylamide

(shown as quaternary salt)

$n = x + y$

y = 5% to 100% and refers to the ionic character

n = degree of polymerisation

the mineral processing industry for over 25 years. Such flocculants are widely used for enhancing conventional thickening/clarification rates and filtration and centrifugation properties (10).

2.1.2.2 Mechanisms of flocculation

Four mechanisms have been proposed to account for the action of high molecular weight polymeric flocculants. These are:

a) Bridging - the bridging mechanism, first proposed by Ruehrwein and Ward (11) is the most widely accepted theory and is illustrated in Fig. 2.4.

The polymer chain is adsorbed onto the individual particle surface at only a few points of attachment, with the bulk of the chains projecting into solution, in "loops and tails", for contact with other particles. For effective flocculation to occur the polymer must have an extended configuration in solution, preferably with an end-to-end distance of > 1000 Å (12) (which may be influenced by factors such as pH, ionic strength and presence of polyvalent counterions). The polymer must also be adsorbed on the mineral by multifunctional groups. This attachment may take place by either chemical forces (section 2.1.2.4), operating at short distances, or physical forces (section 2.1.2.3), extending over longer distances.

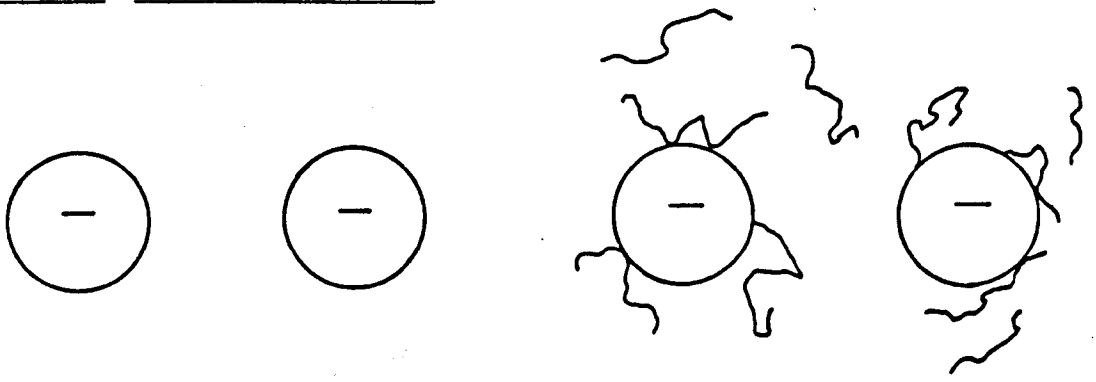
b) Depletion or Volume Restriction Flocculation - this is shown diagrammatically in Fig. 2.5 and has only recently been proposed (13, 14, 15). It suggests that stability arises from the depletion of the concentration of free polymer between the surfaces

of the particles, due to the effective diameter of the polymer coils exceeding that of the interparticle distance, when in close proximity. In a good solvent, even closer approach of the particles is achieved by a further reduction of the segment concentration between the particles, resulting in virtual exclusion of polymer molecules between the surfaces.. Thus the interparticle space is occupied by almost pure solvent which, energetically, favours even closer approach, because it results in the mixing of almost pure solvent with polymer solution.

c) Charge-Patch Flocculation - proposed by Gregory (16) in order to account for the action of low molecular weight cationic polymers, on latex particles. Because of strong ionic interactions when adsorbed onto negative particles, polycations may adopt a rather flat configuration, without loops and tails, thus minimising bridging flocculation. If, however, the cationic polymer were to adhere to only one side of the particle, attraction between it and other negatively charged particles would result, thus bringing about aggregation. This is shown diagrammatically in Fig. 2.6. Previous work however (17), had indicated that bridging played an important role in the action of cationic flocculants.

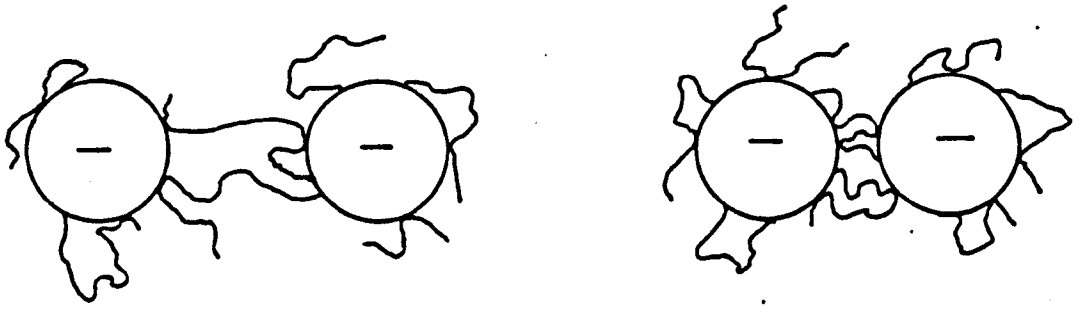
d) Hybrid of Bridging and Depletion - this has been discussed by several authors (18, 19, 20) and involves incompatible interaction of free dissolved polymer with strongly adsorbed or bound polymer.

Figure 2.4 Bridging Mechanism



(a) Two particles in suspension

(b) Flocculant adsorbing



(c) Flocculant bridging

(d) Particles flocculated

Figure 2.5 Depletion Flocculation

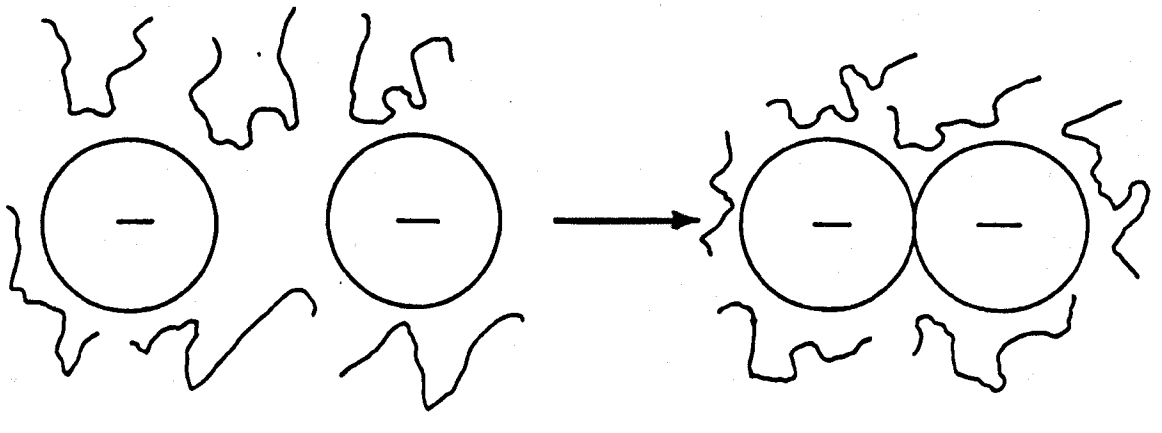
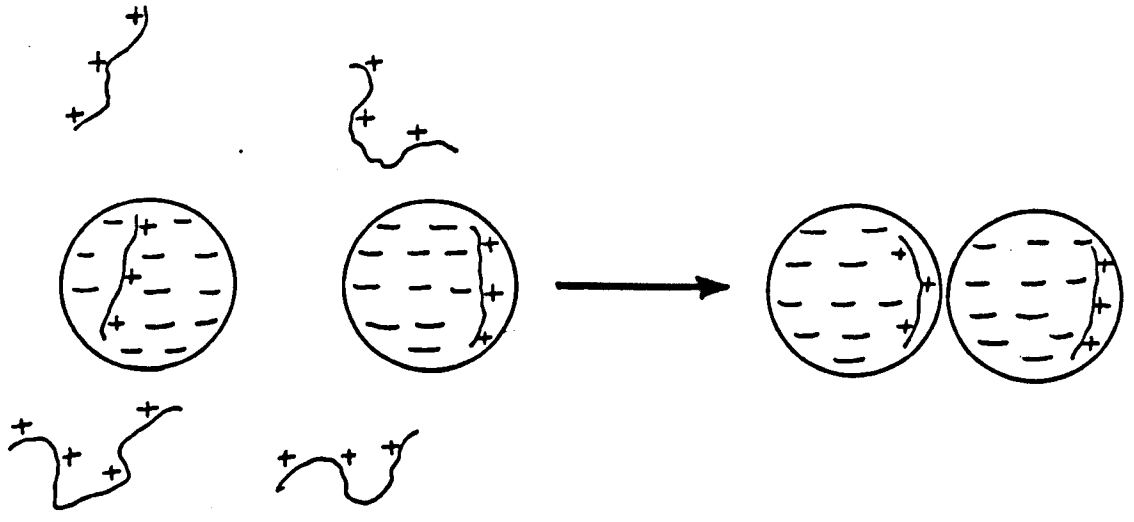


Figure 2.6 Charge Patch Mechanism



2.1.2.3 Physical forces involved in bonding

a) Electrostatic (Coulombic) forces - result in the adsorption of polyelectrolytes onto surfaces of opposite charge, irrespective of their chemical nature. The interaction energy of this bonding may exceed 10 k cal mol^{-1} (21) and as such is practically irreversible.

b) Dipole attraction forces - occur when a dipole, such as is present in the amide groups of polyacrylamide, aligns itself so that its attractive end (of opposite charge to the ion) is attracted to the ionic field of the crystal. Ion-dipole interactions are similar to ion-ion interactions, except that they are more sensitive to

distance and tend to be weaker (< 2 k cal mol^{-1}, 21), as charges comprising the dipole are less than a full electronic charge.

c) London-Van der Waals forces - are due to the attraction of oscillating dipoles in adjacent atoms and have energies of interaction ranging from 2 - 10 k cal mol^{-1}.

d) Hydrophobic bonding - polymeric flocculants that are physically surface active, due to the presence of hydrophobic groups, are attracted to hydrophobic minerals.

2.1.2.4 Chemical forces involved in bonding

a) Chemical bonding - reactions of the polymer group with metallic sites on the solid surface may result in covalent or ionic bonding. The interaction energy of this type of bonding generally exceeds 10 k cal mol^{-1} (21).

b) Coordination bonding - by chelation or complex formation leading to polymer attachment at the surface. This is achieved with specifically modified polymers.

c) Hydrogen bonding - this is a very common type of bonding exhibited by organic compounds in which a hydrogen atom is attached to a strongly electronegative atom, such as oxygen, sulphur or nitrogen; as in amides, alcohols and amines. The hydrogen atom, having lost much of its electronic atmosphere, readily accepts electrons from surface atoms of the solids, such as the -OH groups on the hydrated surface of oxide mineral (22). The proton resonates between two electronegative atoms, forming the

hydrogen bond. Although this is a relatively low energy bond, approximately 6 k cal mol^{-1} (23) since an acrylamide polymer of molecular weight one million may form up to 14,000 such bonds, the total energy of attachment per molecule is enormous. Hydrogen bonding is the principle mode of attachment of polyacrylamide type flocculants, especially the non-ionic ones.

2.1.2.5 Factors affecting polymer performance

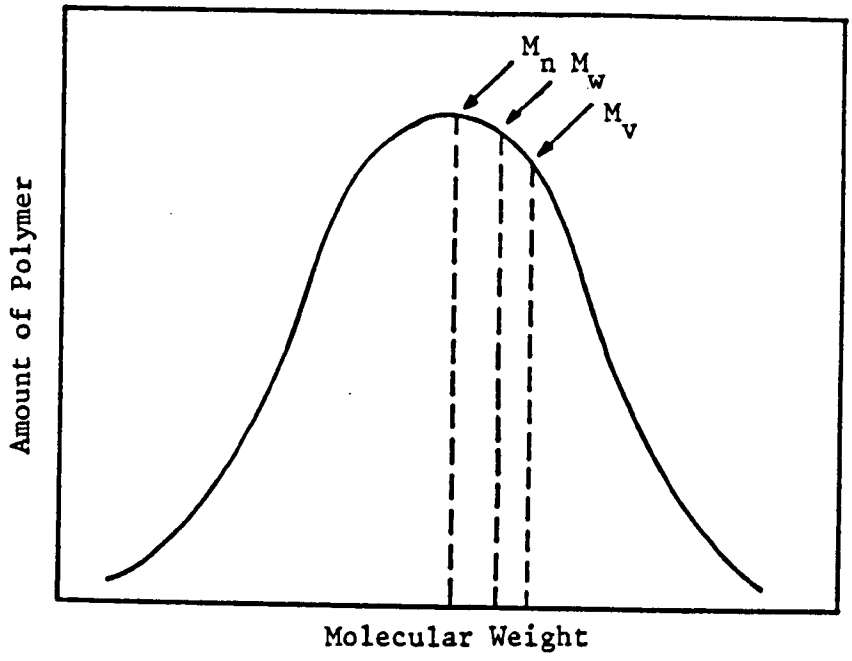
As has been established in section 2.1.2.1, it is possible to produce a range of polymers of various molecular weights, ionic charge densities and even position of charges. Each of these variables may contribute considerably to the polymer performance; as may polymer conformation, dosage and method of addition.

a) Molecular Weight

All synthetic flocculants contain polymer chains of various lengths, and experimentally determined molecular weights can only give an average value. Thesemay be determined by numerous methods, of which, due to the simplicity of the measurement, solution viscosity is probably the most common. Figure 2.7 shows the distribution of molecular weights in a typical polymer.

Whilst two polymers may have the same average molecular weight, due to variations in the molecular weight distribution, their ability to flocculate may be significantly different. As may be seen in Fig. 2.8, although polymers A and B have similar average molecular weights, A has a much wider distribution, with a large number of high and low molecular weight fractions. As a

Figure 2.7 Distribution of Molecular Weights in a Typical Polymer and Relationship Between Various Average Molecular Weights

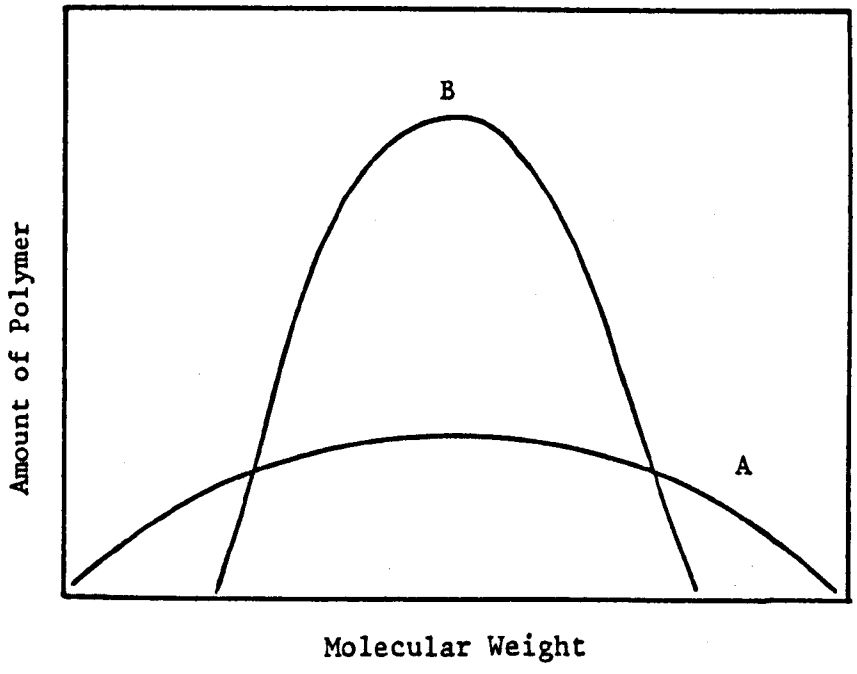


M_n = number-average molecular weight

M_w = weight-average molecular weight

M_v = viscosity-average molecular weight

Figure 2.8 Distribution of Molecular Weights in Two Polymers Having the Same Average Molecular Weight



result, even under identical conditions, the two might be expected to perform differently.

High molecular weight polyelectrolytes have been shown to be extremely powerful flocculating agents for many minerals in aqueous suspension, forming larger, somewhat stronger flocs than their lower molecular weight counterparts (23, 24, 25).

b) Ionic Charge Density

As can be seen in section 2.1.2.1, to various degrees, non-ionic polyacrylamides can be modified to incorporate either cationic or anionic groups. Polymer adsorption and hence flocculation can be affected by the ionic charge density. The charge density most suitable for any particular system depends on the pH and dissolved salts controlling the particle surface charge, zeta potential and polymer configuration.

c) Position of Charges

When two comonomers are reacted together to produce an ionic polymer, depending upon the reactivity ratios of the two monomers concerned, the type of polymer produced will vary. For example, if monomer A (acrylamide) is to be reacted with monomer B (sodium acrylate) in the ratio 1:1, the extremes of polymer which could be produced are:

ABABABABAB or AAAAABBBBB

giving polymer chains of:

Now, although chain length and average charge density are similar, the performance of the two polymers would probably be different.

d) Polymer Conformation

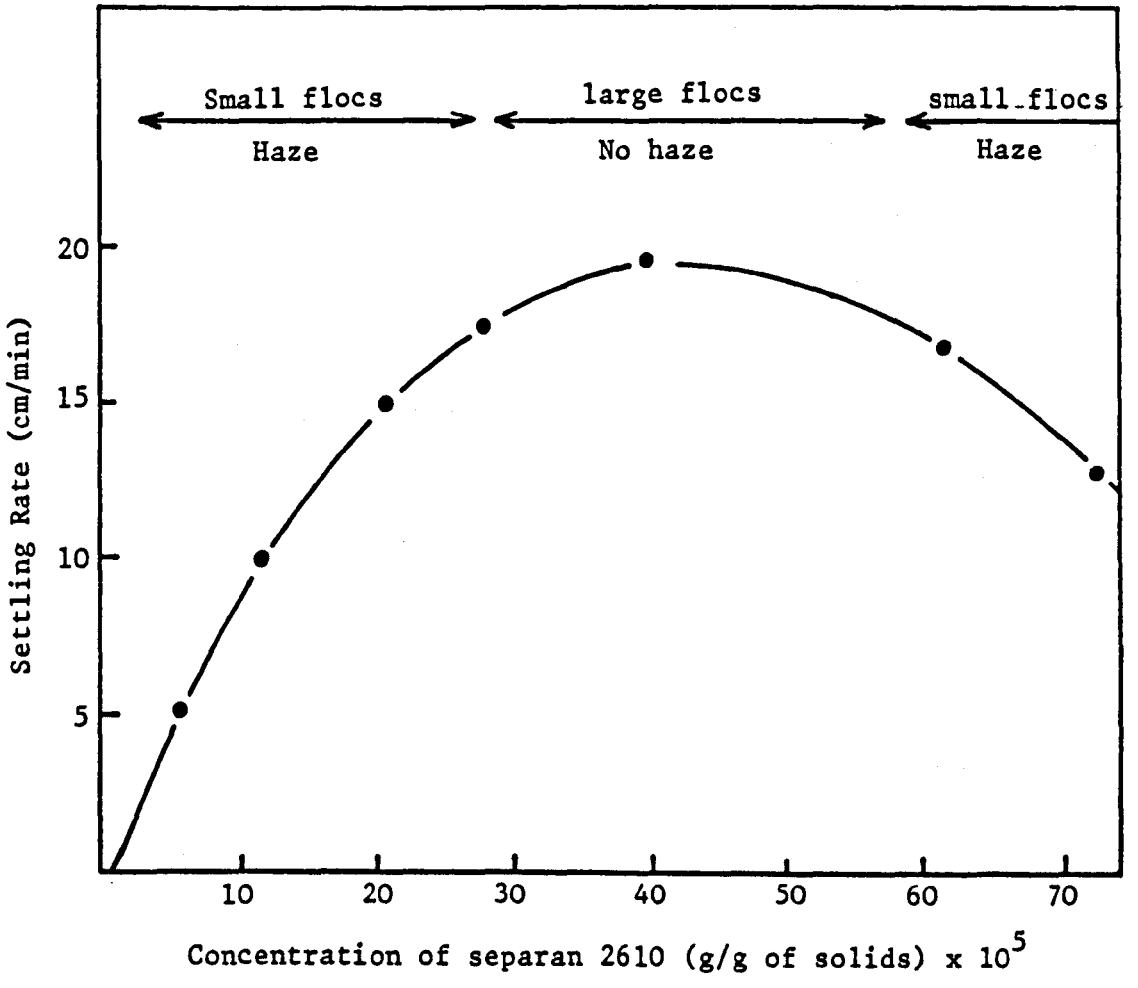
In solution a polymer chain is a randomly coiled mass, the size of the molecular coil being influenced by polymer-solvent interaction forces. In a thermodynamically 'good' solvent, where polymer solvent contacts are highly favoured, the coils are relatively extended, compared with a 'poor' solvent in which they are relatively contracted.

In the case of polyelectrolytes in an aqueous medium when ionisation occurs, mutual repulsion of their charges, causes elongations of the chain far beyond those resulting from the solvent effects of ordinary polymers. Due to their effects on ionisation, the size of the polyelectrolyte coil is also influenced by solution properties such as pH, ionic concentration and the presence of auxiliary inorganic polyelectrolytes. Their effects are complex since they produce simultaneous effects in the nature of the polymer as well as in the particle surface (see also section 2.3.1.5).

e) Polymer Dosage

The optimum polymer concentration has been defined as that concentration for which utilisation of extended segments is at a maximum (26); this may be regarded as approximately half surface coverage of the solid by a polymer. As the fraction of surface covered increases, the chances of extended segments adsorbing and bridging decreases (26, 23) and complete surface coverage of the solid by the polymer may result (see Fig. 2.9 (27)). In general, as the molecular weight of the polymer is increased so are both the settling rates of the solids and the dosage required for optimum conditions (23).

Figure 2.9 Effect of Flocculant Addition on the Settling Rate of a 5% Solids Quartz Pulp



f) Method of Addition

The irreversible, rapid adsorption of many polyacrylamides, coupled with their high affinity for a solid surface all contribute to their effectiveness. With these factors however, in order to obtain maximum flocculation, the technique of flocculant addition is necessarily very important. If a flocculant is added to a pulp either without agitation, or as a relatively concentrated solution, local overdosing results, efficient flocculation is not achieved and in fact much of the pulp remains dispersed. To obtain more uniform distribution, without wastage, the addition of the reagent solution with gentle agitation is most effective (28). This produces the required particle collisions essential for floc formation.

g) Effect of Agitation

Flocs produced with high molecular weight organic polymers are usually quite weak and easily broken by shear forces (29). Increasing intensity of agitation during polymer addition causes decreased polymer adsorption and floc size (27). Continuing agitation following floc formation, can result in the breakdown of the flocs and almost complete coverage of individual particles by the polymer (28). This has been explained more fully to be as a result of the extended segments of the polymer bridges "curling" back, adsorbing onto solid sites and causing a contraction of the floc. Due to the reduction in bridge lengths, the floc is then less resistant to shear and begins to break up thus exposing fresh surfaces onto which further polymer may adsorb (redispersion) (30).

It is therefore generally accepted that the following three rules, applied to polymer addition, will produce the most effective conditions for flocculation (31):

i) Continuous addition of polymer, without further mixing when complete.

ii) Time and intensity of agitation must be regulated to achieve maximum promotion of floc formation, whilst minimising floc degradation.

iii) The initial stock concentration of polymer is not critical provided sufficient mixing accompanies the addition; although more dilute solutions may mix more thoroughly (28).

2.1.2.6 Examples of polymer adsorption onto mineral surfaces

The physical and chemical forces present in the bonding of polymers were described in sections 2.1.2.3 and 2.1.2.4. In order to obtain the necessary adsorption of a particular polymer onto a specific mineral surface a knowledge of the type of bonding likely to result is essential. The following section outlines some of the mechanisms involved for specific systems and illustrates the complexity of the processes involved.

Electrostatic attractions are largely responsible for the adsorption of polycations onto clays (12) at their negative faces and for the adsorption of anionic polyacrylamides, onto positively charged synthetic corundum, fluorite, barite and calcite (32).

Yarar and Kitchener (33) however, suggested that the adsorption of anionic polymers onto calcite, may be a chemisorption process, because of the precipitation of these polymers, by Ca^{2+}, as calcium salts. A chemisorption process is also indicated for the adsorption of polyacrylic acid at the surfaces of other calcium containing minerals, such as scheelite and limestone, because of the formation of insoluble calcium acrylate (34).

In neutral or alkaline media, the carboxylate groups of polyacrylamides facilitate interactions to cationic centres on particle surfaces. Positively charged hydrolysed aluminium ions can act as anchor points for the adsorption of non-ionic and anionic polyacrylamides, to the negative surface of kaolinite suspensions (36). Filtration and dewatering characteristics of Kimberlite clay slimes, using an anionic polymer, were considerably improved with the introduction of magnesium sulphate (36). This use of coagulant and flocculant together is seen to moderate the repulsion between polyelectrolyte chains and clay particles to the point where sufficient strength of adsorption and most effective bridging power is obtained. Reduction of the zeta potential of clay particles (and possible mean charge density of polyelectrolyte) would account for this.

Yarar and Kitchener (33) used Ca^{2+}, Cu^{2+}, Co^{2+} and Fe^{3+} as "activating" metal cations in the flocculation of quartz with anionic polymers. They concluded that; i) divalent cations reduced repulsions between anionic polyelectrolytes and negatively charged mineral surfaces, ii) they permit closer approach between similarly

charged particles or (iii) they interact with carboxylate ions and surface silicate ions to form an electrostatic link.

Data available suggests that the flocculation of fluorite by a non-ionic polyacrylamide is the result of the interaction of dipolar groups with the electrostatic field of the crystal lattice (37).

Hydrophobic bonding explains the adsorption of amphipathic polymers, such as incompletely hydrolysed polyvinyl acetate, at oil/water interfaces and on hydrophobic solids such as graphite. A combination of hydrogen bonding and hydrophobic association is thought to be responsible for the adsorption of polyethylene oxide onto silica containing both silanol and hydrophobic groups (eg. methyl or siloxane) (38).

A number of water soluble polymers of high molecular weight, incorporating complexing or chelating groups for heavy metal ions, have been prepared and tested as flocculants. Attia and Kitchener (39) achieved a successful separation of various copper minerals from gangue using the chelating polymer, polyacrylamide-glyoxal bishydroxyanil (PAMG)

Hydrogen bonding plays a major role in the adsorption of polyacrylamides onto mineral surfaces, and has been the subject of numerous studies.

Attia and Fuerstenau (40) concluded that the adsorption of a slightly anionic polyacrylamide onto fluorapatite and hydroxyapatite results mainly through hydrogen bonding. This occurs between the

OH group of the apatite surface and amide groups of the polyacrylamide molecules; electrostatic forces playing only a minor part. Similarly, polyacrylamides (non-ionic or ionic) adsorb onto haematite primarily by hydrogen bonding between surface oxygen groups and polymer amide groups (41). Electrostatic attractions again play only a secondary role.

Infra-red spectroscopy was used to verify the presence of hydrogen bonds in the adsorption of polyacrylamide onto silica (42) and also polyoxyethylene adsorption onto coal. The latter occurs through interaction of ether oxygens of polyoxyethylene and hydroxyl groups on the coal surface (43).

Hence it can be concluded that although hydrogen bonding, especially with polyacrylamides, plays a major role in adsorption many other mechanisms, such as hydrophobic and electrostatic interactions, also have a part to play. A thorough knowledge of the system being studied is thus necessary before attempting to explain polymer adsorption.

2.2 ELECTROKINETIC EFFECTS

2.2.1 Electrical Double Layer

When two phases, namely a solid and a liquid, are placed in contact, a difference in potential generally develops between them. The region between the two adjoining phases is marked by a separation of electric charges, so that near to, or on the surface of the first phase there is an excess of charges of one sign, with a balancing

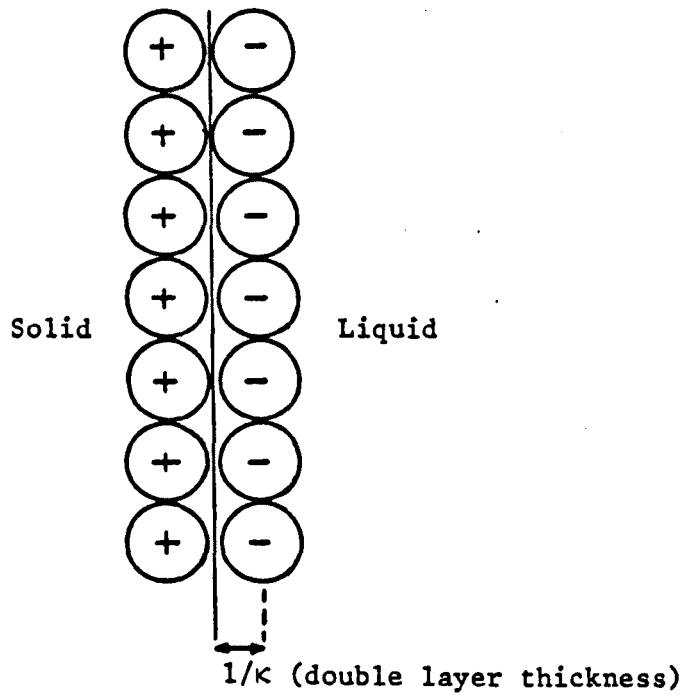
charge distributed through the adjoining surface regions of the second phase. This arrangement of charges is referred to as the electrical double layer at the interface.

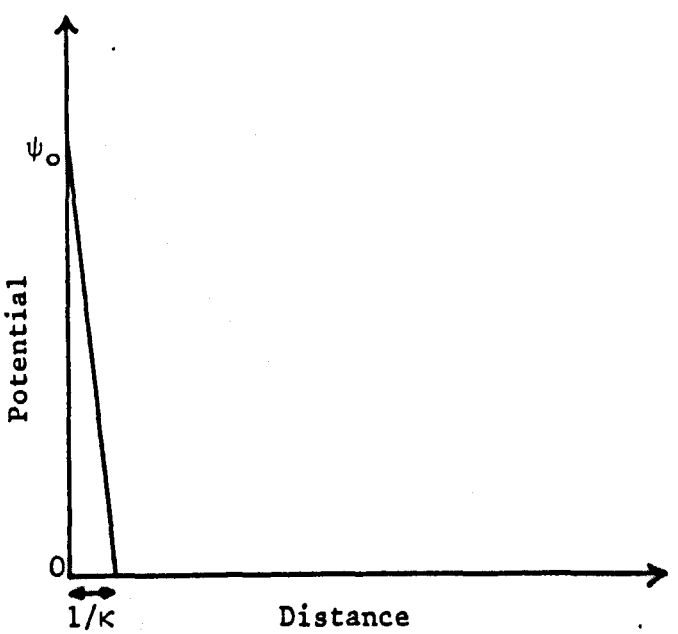
The theory of the electrical double layer deals with the distribution of counter ions (oppositely charged) and co-ions (of similar sign) around the charged surface, in contact with a polar medium, and thus with the magnitude of electrical potentials occurring in this region. This is an important phenomena in the interpretation of many experimental observations concerning the electrokinetic properties, ion exchange, adsorption, flotation and flocculation of such charged colloidal systems.

Helmholtz first introduced the concept of the electrical double layer in 1879 (44). He proposed to treat the excess of electronic charges in the solid as a surface charge, with the counter-ions in the electrolyte behaving as a charged parallel plate at the surface. This arrangement is shown in Fig. 2.10.

However, thermal motion of ions in solution, which would prevent such a rigid arrangement of positive and negative charges, made this model inadequate.

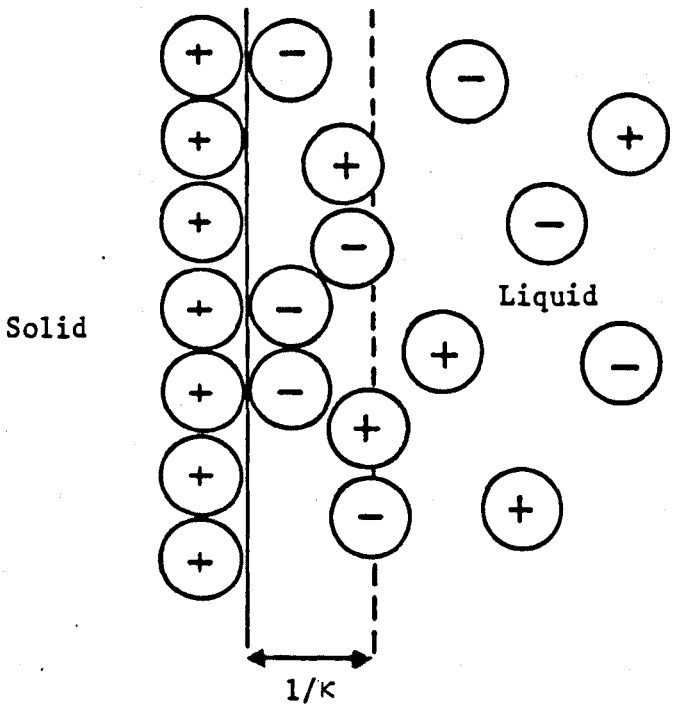
Gouy (1910), and later Chapman (1913) (44) realised the importance of thermal motion and suggested a balance between electrical forces, tending to attract counter-ions and repel co-ions, and the thermal motion, which tends to produce uniform distribution of these ions. The combined effect of these forces produces a diffuse distribution of ions in solution, relative to the solid surface. Figure 2.11 illustrates this.





Variation of potential with distance from solid-liquid interface

Figure 2.10 The Helmholz Model



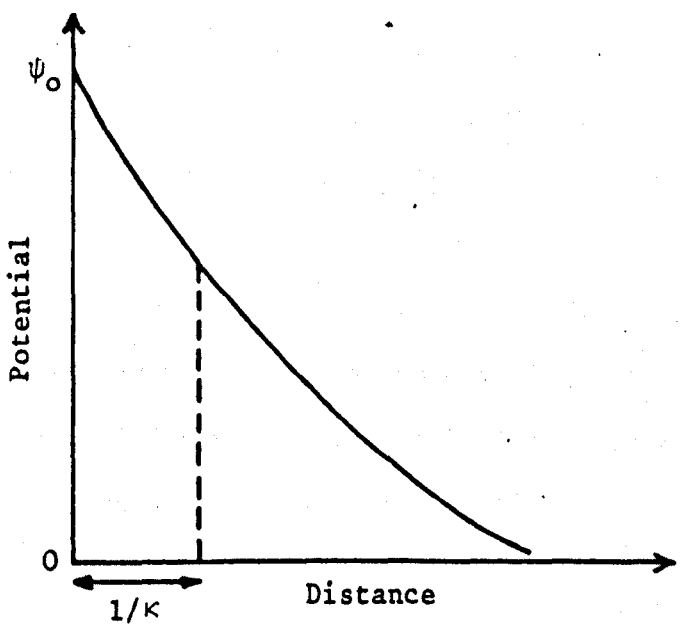


Figure 2.11 The Gouy-Chapman Model

The Gouy-Chapman theory also suffers from defects, which lead to absurdly high ionic concentrations being calculated at the surface. Hence the structure of the double layer is best described by a combination of the two previously proposed models.

In 1924 Stern (44) suggested that some ions in the double layer were not subject to thermal motion, but were, in fact, adsorbed at specific sites in the interface, giving rise to two layers close to the surface. A strongly attached compact layer of counter-ions at the surface, which were able to overcome thermal agitation, and a diffuse Gouy layer further from the surface. This is shown in Fig. 2.12.

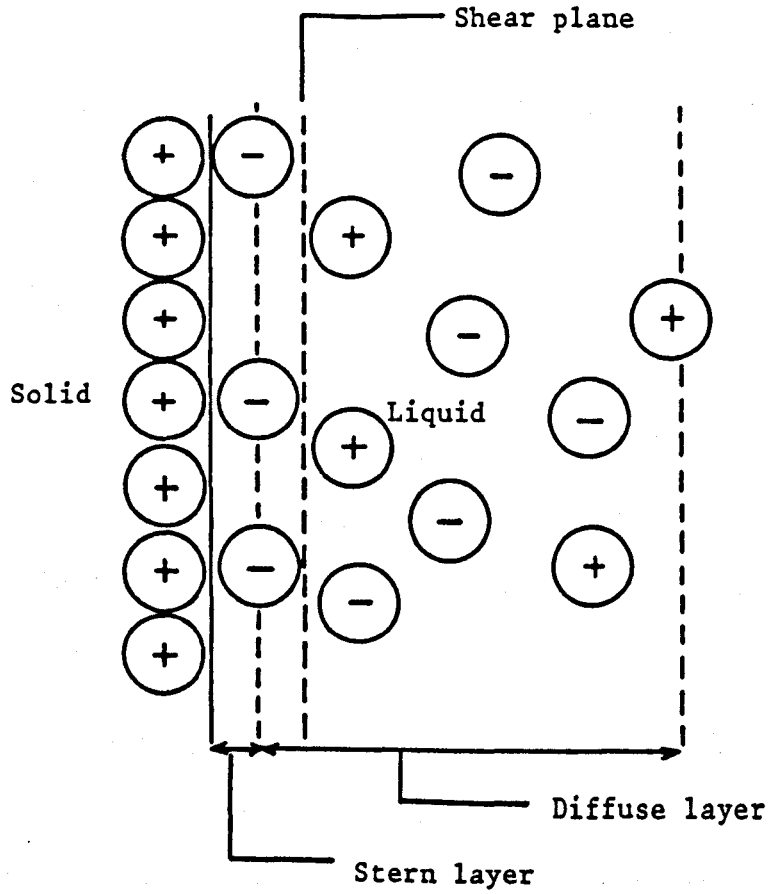
It is important to note that the distance of the electric charge from the surface is the most important factor in describing the electrical double layer.

Depending on the way in which motion is brought about, four distinct electrokinetic effects may be produced (45):

a) Electrophoresis - when one phase consists of a liquid or gas in which the second phase is suspended as particles of solid or liquid, particles can be made to move by applying an electric field across the system.

b) Electro-osmosis - when the solid remains stationary and the liquid moves as a result of an applied potential gradient.

c) Streaming potential - when a liquid is forced to move through a capillary or porous plug, under a pressure gradient.



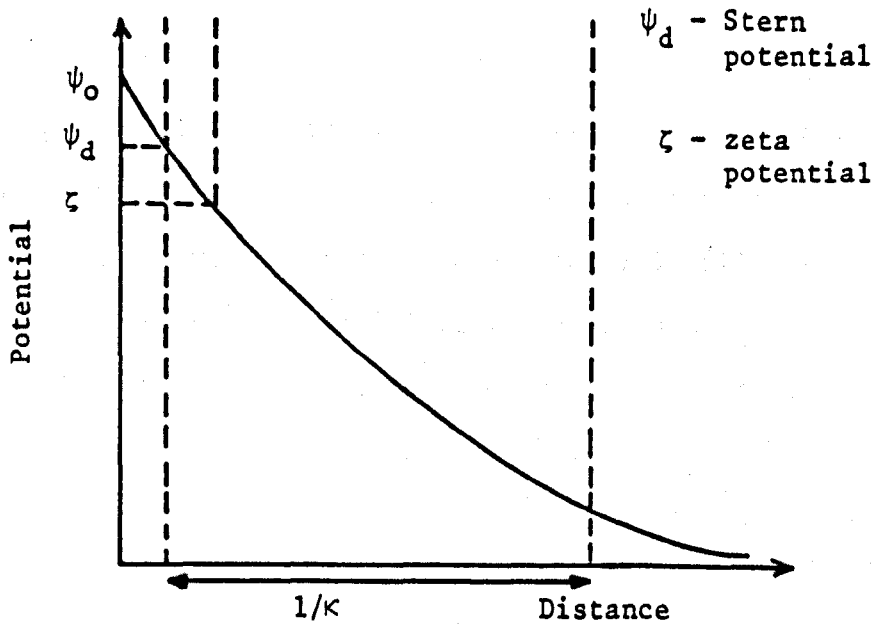


Figure 2.12 The Stern Model

d) Sedimentation potential - when charged colloidal particles are allowed to settle, or rise, through a fluid by gravitation or in a centrifugal field.

2.2.2 Zeta Potential (ζ)

In each case of the electrokinetic effects above, a plane of shear results between the double layer and the medium involved. The zeta potential may be defined as the potential at this shear plane, between the fixed layer of liquid adjacent to the surface and the liquid forming the bulk solution.

However, the location of the shear plane is not well defined and has been considered by several authors. Overbeek (46) considered two cases; one with the shear plane located in the Gouy part of the double layer, the other with the shear plane located in the Stern layer. Hunter and Alexander (47) concluded, in a study on kaolinite, that it lay 10 Å from the kaolinite surface.

The zeta potential is related to both the surface potential (ψ_o) and the Stern potential (ψ_σ) and, if conditions are controlled, changes in the zeta potential may be considered to reflect changes in these potentials. However, a change in zeta potential will only reflect a change in surface potential if ionic strength remains constant and no specific adsorption occurs other than by potential determining ions.

Relationships between surface potential and zeta potential are given in Figs. 2.13, 2.14 and 2.15.

2.2.2.1 Isoelectric point (IEP) and point of zero charge (PZC)

When a solid is dissolved both negative and positive species are present in solution. The situation where the two charges are electrically equivalent is called the isoelectric point (IEP). Similarly at the solid-solution interface when there is equal adsorption of H^+ and OH^- ions, the point of zero charge occurs (PZC). Zeta potential measurements are often used to determine the PZC of a mineral, although other methods are available.

The origin of the surface charge on minerals in water is of great importance in the mineral processing industry, since a good deal of the flotation, rheological and aggregation behaviour of mineral pulps is influenced by this charge. Much of the understanding of the charging mechanism has been developed from the results of electrokinetic measurements of the PZC and the effect on zeta potential of potential-determining ion concentrations.

Healy (48, 49) and coworkers, Parks (50) and Van Olphen (51) are among those who have developed theories for the origin of surface charge.

Numerous studies have been carried out using zeta potential data as a tool for investigations into flotation behaviour (52) dewatering (53) and settling rates (27).

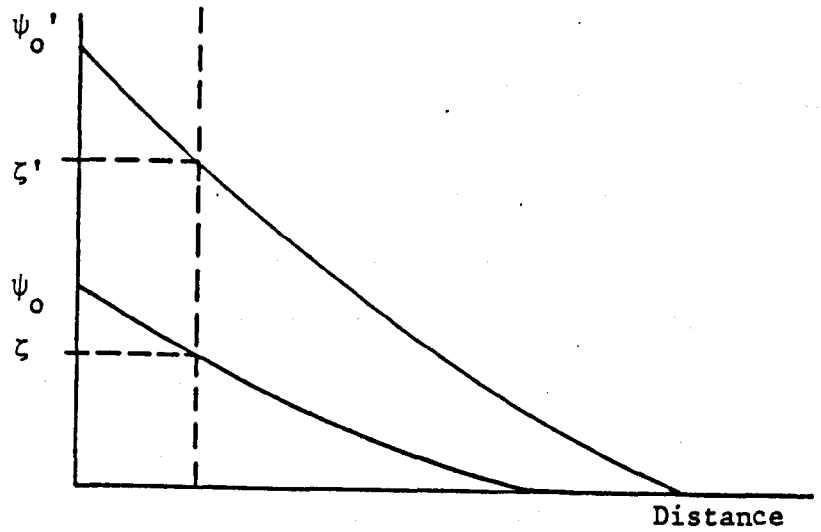


Figure 2.13 Two Different Values of Surface Potential at Constant Ionic Strength

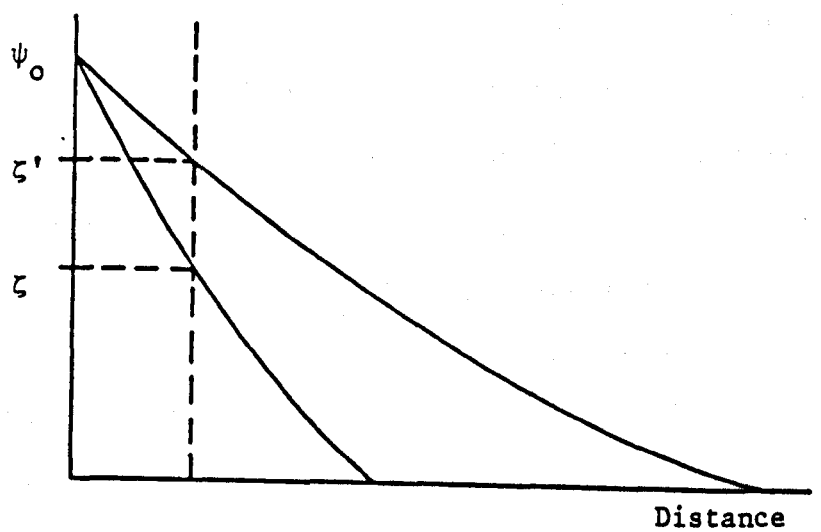


Figure 2.14 Two Different Values of Ionic Strength at Constant Surface Potential

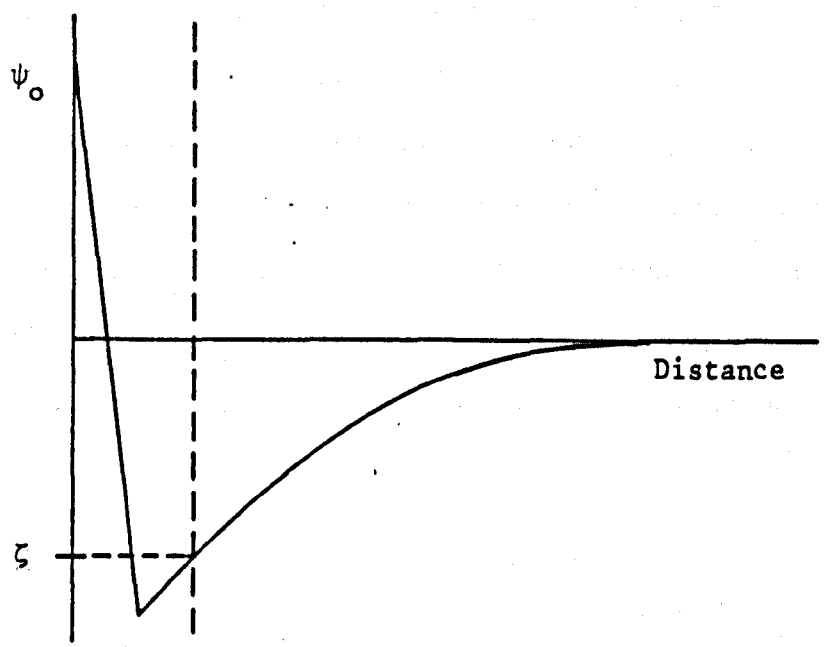


Figure 2.15 Effect of Specific Adsorption on Zeta Potential

2.2.3 Application of Zeta-Potential Data in Flocculation Studies

Since flocculation is generally accepted as being a result of the bridging mechanism, electrical double layer interactions are minor and as such electrokinetic techniques have not played such a large role in this particular area. However, the adsorption of charged polymers at charged mineral surfaces is likely to cause changes in the zeta-potential which may affect the mechanism of polymer flocculation.

Kuzkin et al (32), in a study of relationships between zeta potential, polymer adsorption and subsequent flocculation, showed that zeta-potential changes follow adsorption. In addition, polymer adsorption, and to some extent bridging, are influenced by both surface and polymer charge. Similarly Healy (27) noted that although a reduction in zeta-potential to around -15 mV followed the adsorption of hydrolysed polyacrylamide onto quartz, this was in fact a subsidiary mechanism to that of bridge formation.

Some negatively charged polymers appear not to flocculate strongly negatively charged solids such as quartz (33). This may be due to the fact that electrostatic forces overcome any hydrogen bonding forces present. The addition of divalent or trivalent metal cations produced effective flocculation. In the same study, extensive use of zeta potential data, when investigating quartz, calcite and galena systems, showed that this knowledge may provide grounds for predictions regarding conditions for their separation.

2.2.4 Investigations into Coal and Shale Using Electrokinetic Techniques

Investigations into coal using electrokinetic techniques are more widespread than those involving shale, due possibly to the imprecise nature of the latter. Shale comprises mainly kaolinite, illite, chorite, quartz (54) and also some iron and aluminium oxides. Of these, from an electrokinetic viewpoint, quartz has received more attention, and this has helped to develop the theory of the origin of the surface energy charge on simple oxide minerals (55, 56, 57, 58).

On the other hand, the composition of coal (metamorphosed plant and mineral matter) is less ambiguous, comprising mainly carbon, oxygen and hydrogen. The hydrophobic nature of coal is increased on increasing rank (i.e. degree of metamorphosis) from brown coal ($\simeq$ 60% carbon) to anthracite ($\simeq$ 95% carbon). Depending on its rank, the zeta potential of coal is found to be negative above pH values of between 2 to 6 (53). Burdon and Mishra (59) however, have reported that, for the coals they tested, the zeta potential was negative at all pH values. This could be attributed to various factors such as difference in composition, degree of oxidation and possibly even to some extent, sample preparation.

Similarly for shale, above a pH of about 4, Beckett (60) noted that the zeta potential at the interface changed to a negative mode. Adsorption of calcium ions at neutral pH tended to allow coagulation to occur, since it was followed by a reduction in the size of the negative zeta potential.

Following his discovery of similarities between electrokinetic results of bituminous coal, and those from double layer phenomena characteristic of oxide materials, Campbell (61) suggested that coal comprises either an outer oxide layer, or an outer layer having oxide-like characteristics.

Slime coatings of coal by clay in flotation pulps, using zeta potential measurements, was the subject of a study by Jowett (54). Hydrophobic coal particles were rendered hydrophilic by clays, imparing flotation recovery. The zeta potentials of both coal and slimes were found to be negative, although the edges of the slimes were, in fact, positive. This resulted in electrostatic attraction been coal and clay particles. Addition of phosphate ions, which are negatively charged, neutralising the positive edges, was followed by an increase in the zeta potential of both species, preventing slimes coating by producing more effective repulsions.

Miller and Deurbrouck (62) observed that the flocculation of coal slimes became more effective as the naturally occurring negative zeta potential approached zero, thus zeta potential control ensures optimum performance of any flocculant.

In studying the effects of oxygenated groups on coal flotation, Ayatallahi (63) found that at neutral pH, the higher the percentage of reactive oxygenated groups at the coal surface, the higher the negative zeta potential. This resulted in a poorer response to flotation.

Bethell (64) investigating chemical filtration aids found that the sign of the zeta potential was reversed on adsorption of an aliphatic diamine compound, at the coal-water interface. However,

the most significant increases in product yield and reductions in cake moisture content, over conventional systems, were not apparent at the I.E.P. of this system. This was due to a combination of two complicating factors at this dosage; namely the formation of dessication cracks in filtration cakes and production of large volumes of very stable froth. Zeta potential data of various mineral suspensions, has therefore lead to numerous conclusions being drawn with respect to its influence on, in particular, flotation and filtration and, to some extent, flocculation.

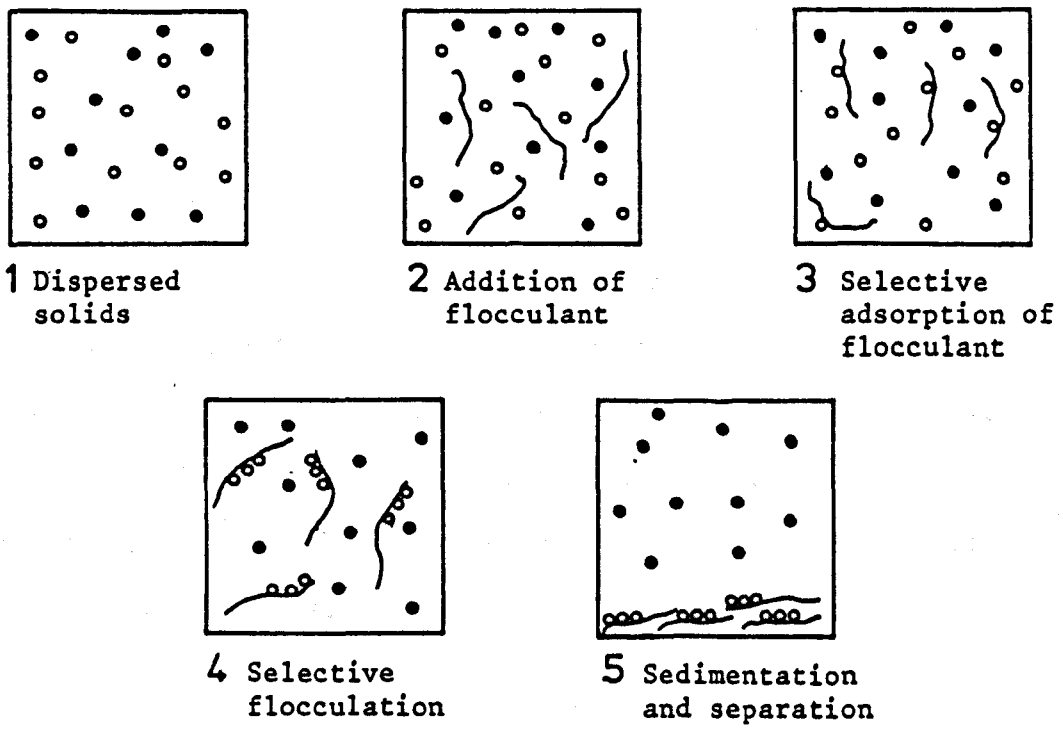
2.3 SELECTIVE FLOCCULATION

The mineral processing industry has employed non-selective flocculation for many years and a logical progression of this would appear to be its selective use involving the separation of one mineral from a mixed mineral slurry.

Successive stages in the selective flocculation process are shown diagrammatically in Fig. 2.16.

It may be achieved by the use of either a commercial polymer, which may or may not exhibit selectivity towards specific minerals, or a modified polymer, containing a chelating group, introduced specifically to bond to one particular mineral surface. The selectivity of any system may be further enhanced by the introduction of a dispersant or surfactant.

Figure 2.16 Selective Flocculation



2.3.1 Parameters Influencing Selective Flocculation

Successful selective flocculation may be affected by any of the following factors:

i) Mineral composition of the suspension.

ii) Particle size distribution.

iii) Type and dosage of dispersant.

iv) Dispersion/conditioning time allowed.

v) Type and dosage of flocculant.

vi) Method of flocculant introduction.

vii) Type and dosage of modifying agents (surfactants).

viii) Solids concentration.

ix) Chemical composition of the water.

x) Temperature of the system - complex effects.

xi) Order of reagent addition.

Some of these factors are discussed in more detail in the following pages.

2.3.1.1 Dispersants

It appears that before selective flocculation can occur, the mixed pulp must initially be in a dispersed state (25), so that all particles are essentially separate and no heterocoagulation occurs. The primary function of the dispersant is therefore to reduce gravitational settling and aggregation rates of individual particles to very low or zero values.

Dispersion may be achieved by the use of either:

(a) Commercially available dispersants - these include reagents such as sodium hexametaphosphate (Calgon), sodium tri-poly-phosphate, tetrasodium pyrophosphate, sodium silicate and sodium carboxymethylcellulose (CMC). These have all been utilised for various mineral combinations (65, 66, 67).

or

(b) Selective dispersants - this approach is based on an idea put forward in work (68) on chelate-forming organic compounds as flotation reagents. Selective dispersants can be prepared by incorporating chemical groups, selective towards one mineral in a mixed suspension, into less selective dispersants. They can often be used in conjunction with a normally unselective flocculant. Attia (69) has prepared such a reagent by the introduction of

phenolic groups, selective towards magnesium and calcium bearing minerals, into Dispex N40 (a polyacrylate). Testwork showed that this reagent exhibited selective dispersion and depression behaviour towards calcite and dolomite, and to a lesser extent, toward feldspar. Results confirmed that, compared with the unmodified dispersant, more effective selective flocculation of copper minerals, from mixtures of calcite, dolomite and feldspar, was achieved.

Indeed it may be said that selective flocculation could also be described by the term selective dispersion, thus inhibiting flocculant adsorption on one mineral surface rather than promoting its adsorption onto another. Flocculant adsorption has been inhibited in numerous cases by electrostatic repulsion (25), pre-adsorbed species (33) and by 'ageing' of quartz (70).

Since it is difficult to predict the precise influence a given dispersant may exert on a given mixed mineral suspension, the optimum conditions necessary to achieve the most stable dispersion conditions must be obtained by experimental investigation. However, a knowledge of the surface and dispersion behaviour of each component, with various reagents, will provide useful guidelines.

2.3.1.2 Flocculants

Following successful dispersion of a mineral pulp, selective flocculation may be achieved by use of:

(a) Commercially available polymers - these often have some inherent selectivity for a particular mineral when used in conjunction

with a non-selective dispersant. Several authors (25, 71, 72) have achieved selectivity, in various degrees, with such polymers. In fact for any mineral suspension, under given conditions, some flocculants clearly function better than others, by adsorption onto suitable sites of a particular mineral.

Surface potential acts in at least two modes (73):

i) by controlling the degree of adsorption of any charged ion-containing flocculants.

ii) by controlling the degree of repulsion between similarly charged particles within the floc.

These two factors are highly relevant since, a high degree of repulsion between particles may result in the formation of weak flocs, or inhibit flocculation completely. On the other hand oppositely charged particles could undergo strong adsorption, with a resultant loss of "loops and tails" for flocculation. Also, intramolecular bonding between carboxylate groups of hydrolysed polyacrylamides, which cause, in acid solution, the molecule to coil and decreases the possibility of bridging, may result as the number of carboxylate groups is increased.

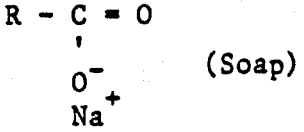
(b) Chelating polymers - in order to produce a more selective flocculant than those commercially available, the idea of incorporating a chemical group into a polymer was suggested. This group would possess a strong affinity for ions on the mineral to be flocculated (22). This idea stemmed from the well known selectivity of the various types of flotation collector. For example, xanthates and dithiocarbamates are known as flotation

reagents for heavy metal minerals (e.g. of lead and copper). Such reagents form insoluble compounds with these metals, whereas alkaline earth metals and other cations do not. If such groups were covalently bound to a water-soluble polymer, they could be expected to enhance its adsorption onto heavy metal minerals. The results of Kitchener (39) have indicated that many compounds of this type could be synthesised. Indeed a modified polymer (polyacrylamide glyoxal bis-2-hydroxyamil), when used in conjunction with calgon and dispex, was successful in the selective flocculation of copper minerals from a gangue containing dolomite, quartz, calcite and pyrite.

2.3.1.3 Surfactants

A surfactant is a substance which, when present at low concentrations, is capable of adsorbing onto the surface or interfaces of a system. This results in changes in the surface or interfacial free energies. It comprises a structural group having little attraction for the solvent, known as lyophobic (hydrophobic in aqueous solution) together with a group having a strong affinity for the solvent, known as lyophilic (hydrophilic in aqueous solution). The hydrophobic group is usually a long chain hydrocarbon, whilst the hydrophilic group is an ionic or highly polar species. Depending on the nature of the latter, surfactants are classified as:

A. Anionic - hydrophobic chain carries a residual negative charge.



(Soap)

B. Cationic - hydrophobic chain carries a residual positive charge

$R - NH_3^+ \; Cl^-$ (salt of long chain amine)

C. Non-ionic - no apparent ionic charge on hydrocarbon chain

$RCOOCH_2CHOHCH_2OH$ (monoglyceride of long chain fatty acid)

D. Zwitterionic - both positive and negative charges may be present on the hydrocarbon chain.

$R^+NH_2CH_2COO^-$ (long chain amino acid)

The use of surfactants as adsorbates at interfaces plays a major role in controlling the hydrophobic, or hydrophilic character of the surface. As such surfactants are exceptionally useful reagents in the mineral processing industry for improving the efficiency of selective flotation circuits (64, 74) and, more recently, they have been found to reduce oil requirements in the spherical agglomeration process (75). On a similar line therefore, it may be envisaged that addition of a surfactant, prior to flocculant addition, may improve the efficiency of the selective flocculation process.

Any combination of reagents described in sections 2.3.1.1, 2.3.1.2 and 2.3.1.3 may be used to bring about selective flocculation, but in order to examine the performance of a particular reagent system it is essential that the more important physico chemical variables be identified.

2.3.1.4 Physico-chemical factors relating to the polymer

(a) Polymer Dosage

The most important operating parameter in selective flocculation is probably flocculant dosage, since most systems are very sensitive to overdosing, which inevitably leads to poor recovery grades. Optimum selective flocculation is generally achieved at very small dosages, when surface coverage is small. For example, 1 ppm flocculant was found to produce preferential flocculation of haematite from a haematite/silicate mixture (25). Excess dosages may also result in flocculation (and subsequent entrapment) of all minerals in a slurry.

(b) Molecular Weight

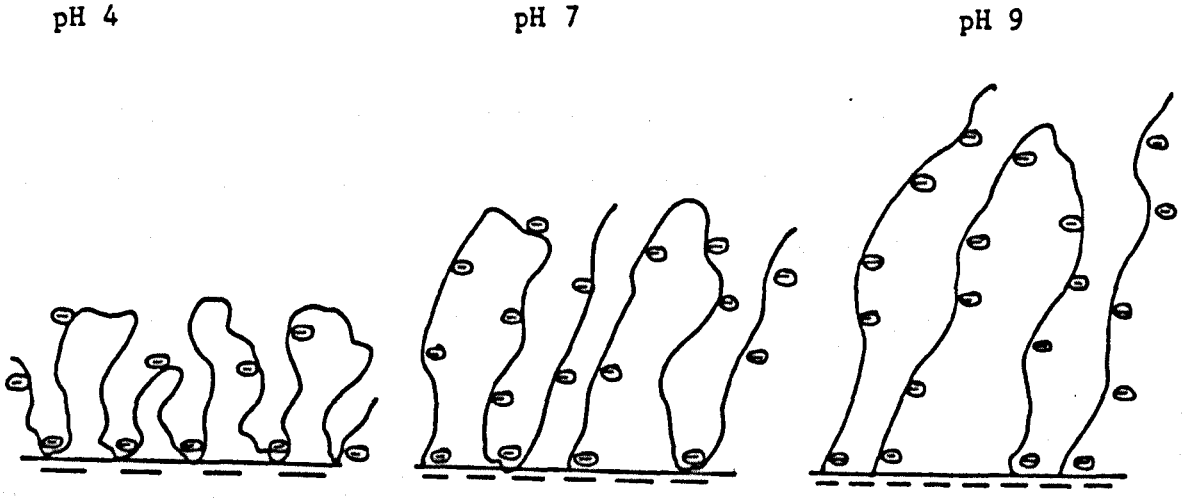
The effects of polymer molecular weight on selective flocculation have not been thoroughly established, although various workers have put forward suggestions. Some (33, discussion) favour low molecular weight products (forming weaker, slower settling flocs) whilst others (33, discussion) have produced effective separations using higher molecular weight products (forming faster settling flocs, but generally leading to increased gangue entrainment).

Other factors already discussed in section 2.1.2.5, namely charge density, method of polymer addition and agitation conditions may also be important with regard to selective flocculation (76, 25).

2.3.1.5 Physico-chemical factors related to the aqueous suspension

To a large extent, the pH of a mixed mineral suspension determines the nature of the interaction between polymer and substrate. Changes in pH are more likely to affect the adsorption of charged polymers, since non-ionics bond by hydrogen bonding alone. For example the effect of pH on the conformation of an anionic polymer at a kaolin/water interface is shown diagrammatically in Fig. 2.17 (8a).

Figure 2.17 Effect of pH on Conformation of Anionic Flocculant at the Kaolin Surface



To obtain the ideal conditions for selective flocculation a balance must be obtained between surface charge and polymer charge, such that adsorption is not too complete as to leave no "loops and tails" for bridging, but, on the other hand, that highly extended "loops and tails" are not favoured thus resulting in large, loose and weak floc formation.

Due to changes in the zeta potential of the particle surfaces and in polymer conformation (77, 78, 79) the effects of varying ionic concentrations are similar to those involved with changes in pH; in that they can either promote or inhibit flocculation. Addition of multivalent inorganic salts, for example, enables effective dispersion of hydrophilic minerals due to an increase in repulsive charges between particles (44).

It has been noted that, in general (80), with increasing salt concentration, both the rate and extent of adsorption also increase. This could be related to changes in the conformation of the polymer in solution, due to the medium becoming a poorer solvent for the polymer.

2.3.1.6 Physico-chemical factors related to the mineral suspension

As the pulp density (solids concentration) of a mixed slurry is increased, an increasing proportion of gangue particles are carried down. This effect, known as entrapment, arises during the rapid formation of a 3D network of floc material which physically entrains dispersed particles, even though no polymer/surface bond

exists (81). Consequently for each system, there is an upper limit to the solids concentration at which acceptable grades and recoveries may be obtained.

Selective flocculation may best be achieved with particle sizes less than 60 μm. On decreasing particle size the dosage of polymer required is likely to increase, due to increasing solid surface area (23) and the ultrafines become susceptible to over-dosing and restabilisation (7).

In a mixture of minerals having different specific gravities, it is easier, though not essential, to flocculate the heavier component, for example galena in a calcite/galena system (33). If the lighter material is to be flocculated then a polymer capable of forming large enough flocs to produce adequate differences in settling rates, must be used, along with an effective dispersant.

It is also worth noting that the surface properties of minerals in a mixture may not be the same as those of the individual minerals (79).

2.3.1.7 Physico-chemical factors related to the surfactant

The adsorption of a surfactant depends upon both its charge and the nature of the substrate, and can generally be divided into three categories:

i) Chemisorption

ii) Electrostatic adsorption

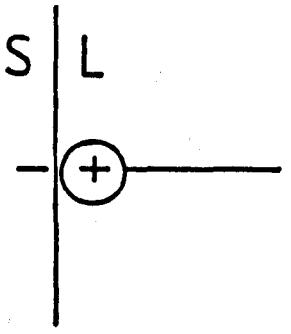
iii) Physical adsorption

Many ideas on adsorption mechanisms have been proposed in the literature, with respect to orientations of surfactant ions at both hydrophilic and hydrophobic sites.

Adsorption at hydrophilic sites

On a hydrophilic surface an ionic surfactant may orientate itself in two ways (82)

(a)

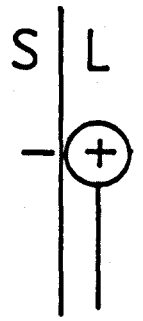


Vertical orientation

The hydrocarbon portion of the surfactant is repellent to the aqueous phase and as such has a tendency to position itself as far as possible from the normal aqueous phase. However due to the fact that the attraction between water molecules is greater than that between water molecules and the hydrocarbon chain, this situation therefore seems improbable.

A more energetically favourable orientation would be:

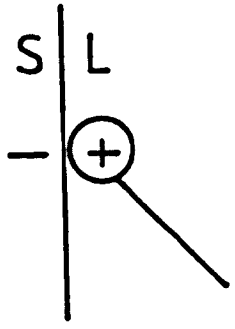
(b)



Horizontal orientation

Here the hydrocarbon chain is positioned close to the solid surface, with subsequent water displacement from the solid surface.

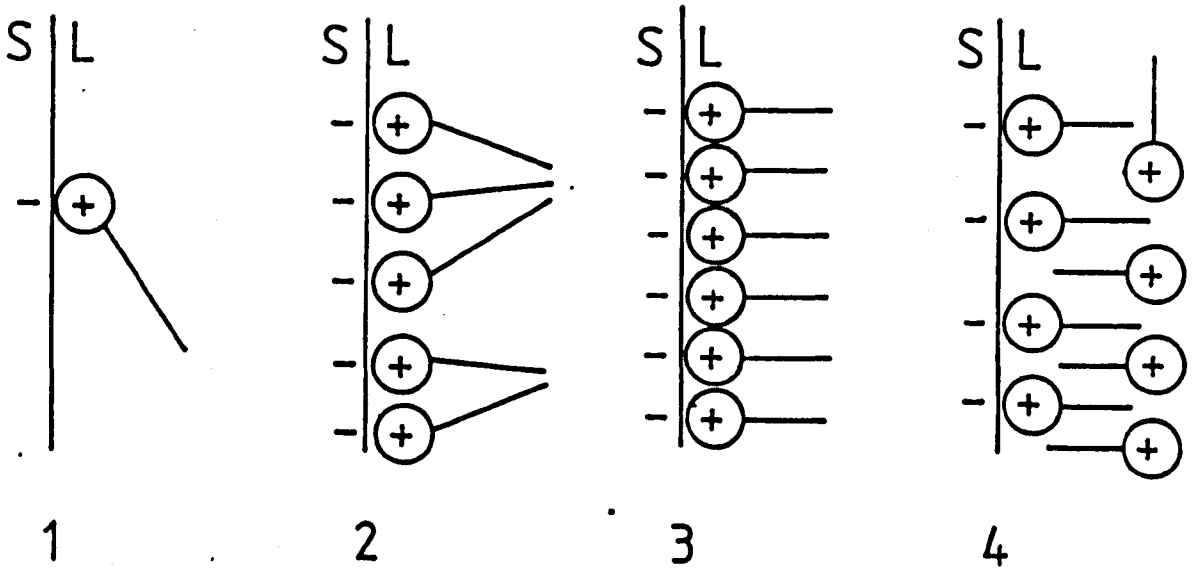
However, it is likely that water is strongly attracted to the surface by ion-dipole interactions, and as such is not easily displaced by the hydrocarbon chain. In fact the water may be so strongly held as to cause an angled orientation;



this being due to an "ice-like" water structure near to the surface (83).

At low concentrations, surfactant ions are individually adsorbed at the surface. As the concentration increases, there is an increase in adsorption, which results from hydrophobic interactions between the hydrocarbon chains. Gaudin and Fuerstenau (58) suggested that adsorbed ions associated in patches at the solid-liquid interface, in a similar way to micelles in the bulk solution. This they termed hemi-micelle formation, producing experimental results in support of their theory. As the concentration increases still further, monolayer formation becomes apparent (84), followed by adsorption of a second layer of surfactant ions in reverse orientation. This is shown diagrammatically in Fig. 2.18.

Figure 2.18 Surfactant Adsorption at Hydrophilic Sites



Formation of region (2) is affected, to a large extent, by the length of the hydrocarbon chain. For example, if the hydrocarbon chain is short, mutual attraction of hydrophobic groups may be insufficient to overcome mutual repulsion of ionic head groups (85). On the other hand, increasing the length of the hydrophobic group increases adsorption efficiency, because the free energy associated with both the removal of the hydrocarbon chain from contact with water, and the tendency to aggregate or adsorb via dispersion forces, is increased with increase in chain length.

Adsorption of non-ionic surfactants has received less attention, but it would appear that hydrogen bonding plays an important role (86).

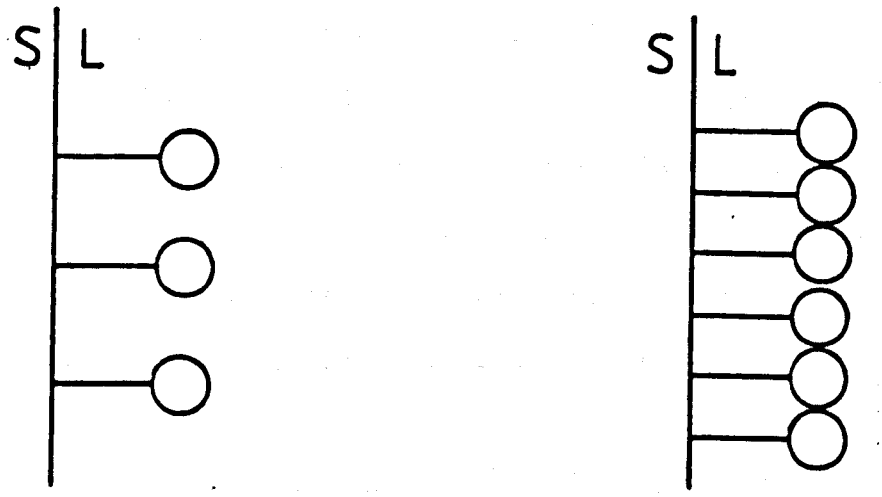
Adsorption at hydrophobic sites

Saleeb and Kitchener (87) suggested that the mode of adsorption of ionic surfactants onto hydrophobic surfaces is affected by the presence of any hydrophilic sites. They studied the adsorption of both anionic and cationic surfactants, at various concentrations, on both "original" and graphitized carbon blacks. "Original" carbon blacks carry weakly acidic oxygen complexes; these act as weak acids providing hydrophilic bonding sites. Graphitization, by heating to 3000°C, removes these sites and induces crystallisation thus providing a surface which behaves like the inert basal planes of graphite.

The following experimental findings lead the authors to conclude that, due to the escape of the non-polar groups from the water phase on graphitized carbon blacks, hydrophobic bonding was the main bonding mechanism, with the surfactant ions horizontally orientated towards the surface. This is shown diagrammatically in Fig. 2.19. Firstly, the fact that on increasing the concentration of surfactant the hydrophobic carbons became hydrophilic and a bimolecular layer was not formed, even in a supersaturated solution. Secondly, saturation of the surface revealed that the area occupied per molecule corresponded to the headgroup of the surfactant.

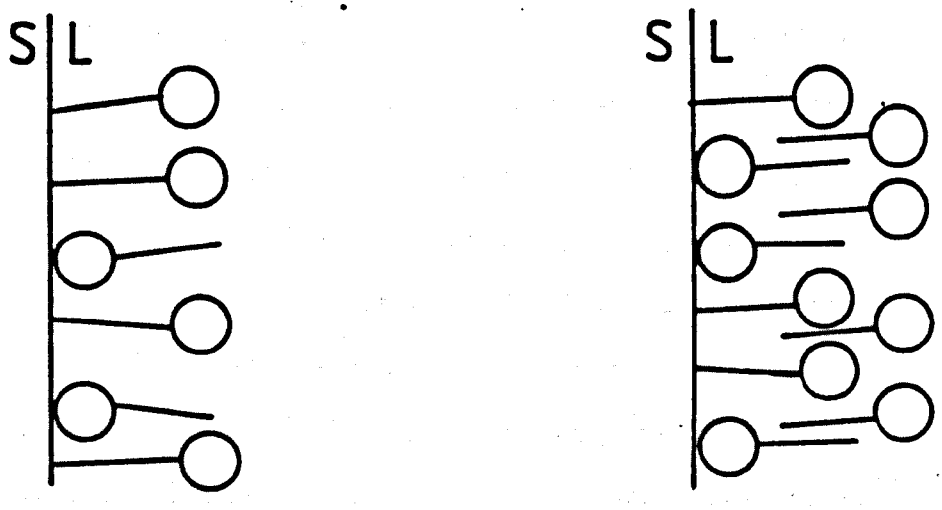
Testwork on the "original" carbon blacks, which possess a charged hydrophobic surface (which may be compared with that of coal), showed that a bimolecular layer was formed. For this to occur it follows that the first layer must be adsorbed in a different manner to that on the graphitized carbon black. It was therefore

Figure 2.19 Surfactant Adsorption on Graphitised Carbon Blacks



proposed that a proportion of the molecules were adsorbed with hydrocarbon chains outermost. Furthermore, interaction with any existing polar groups restricts the freedom of packing of the surfactant, hence orientation is unlikely to be rigidly horizontal. This is depicted in Fig. 2.20.

Figure 2.20 Surfactant Adsorption on "Original" Carbon Blacks



Again as in adsorption at hydrophilic surfaces, increasing the length of the hydrophobic chain increases both adsorption, efficiency and effectiveness.

In order to achieve adsorption of a surfactant, it is necessary that the kinetic energy of the mineral particle and surfactant droplets should exceed the electrostatic repulsion forces present in the system. It is also necessary that "spreading" of the surfactant across the mineral surface should occur. These two barriers may usually be overcome by mechanical forces such as the intense agitation, which generally occurs during the violent mixing of the mineral slurry, prior to the addition of further reagents.

2.3.2 Literature Review of Selective Flocculation

Numerous laboratory separations of minerals by means of high molecular weight polymers have now been achieved and discussed in the literature. These include groups of minerals in various classes: sulphides, oxides, hydroxides, halides, carbonates, phosphates, clays and coals. The following section outlines the conclusions reached in some of these studies.

Calcite, rutile, quartz and alumina were found to show different strengths of adsorption with an anionic polyacrylamide. By providing a sufficiently strongly negative zeta potential it was possible to prevent flocculation altogether, but with consequent adjustments to the zeta potential, selective flocculation of calcite-rutile, calcite-quartz and alumina-quartz was achieved (79). Yarar and Kitchener (33) found that in pure water, mutual coagulation of a quartz-calcite mixture occurred. However, by raising the pH, thereby bringing the zeta potential of calcite into the negative range and avoiding mutual coagulation, an anionic flocculant was found to be selective towards calcite.

The anionic character of a flocculant has been found to be the determining factor with regard to which component is flocculated in a haematite-silicate mixture. Whereas addition of a strongly anionic polymer promoted preferential flocculation of haematite, a mildly anionic polymer showed no selectivity at all and a weakly anionic polymer resulted in selective flocculation of the silicate (25).

Frommer (88, 89) patented a method for improvements in the flotation treatment of iron ores. This involved the selective flocculation of haematite from silica materials using various natural flocculants and the subsequent treatment of the flocculated iron oxides by froth flotation. Improvements in the recovery of iron oxides from siliceous material was consequently achieved.

The beneficiation of complex ores, such as bauxites, was studied by Eigeles et al (71) who concluded that selective flocculation was a promising method especially when used in conjunction with flotation. Commercial quality concentrates, with adequate recoveries, could be achieved with the combined use of sodium carbonate, hydroxide and hexametaphosphate (as dispersants) and anionic polyacrylamide.

Realising that hydroxamine acids have proved good collectors for cassiterite flotation, Claus et al (90, 91) produced modified polyacrylamides, containing these functional groups. This they believed would prove an effective selective flocculation reagent for cassiterite under similar conditions to those successful in flotation. Separation of synthetic cassiterite from quartz in an

aqueous suspension was attempted. High enrichments of cassiterite from low grade ores were in fact possible at pH values from 3.5 - 7. However, poor separation with the cassiterite mineral, as opposed to synthetic cassiterite was achieved; a result which was difficult to explain.

Crysocolla has posed problems for mineral processors for many years, due to its uncertain crystal chemical structure and poor flotation response. Rubio and Goldfarb (92) have carried out dispersion, flocculation and selective flocculation studies on a synthetic mixture of crysocolla and quartz. The indications were that crysocolla could be selectively flocculated employing a non-ionic polyacrylamide, under conditions which leave quartz stably dispersed; that is, in the presence of calgon.

In an attempt to separate crysocolla and malachite from quartz, calcite and dolomite, Rubio and Kitchener (24) attempted to treat the dispersed minerals with a conventional flotation collector. This they believed would render one mineral surface hydrophobic and thus make it amenable to selective flocculation by a suitable polymer attractive to hydrophobic sites. Polyethylene oxide, having good aqueous solubility, high molecular weight and hydrophobic units, was used as the polymer. Their results showed that simple sulphurdisation produced sufficient hydrophobicity on the copper minerals crysocolla and malachite and no advantage was gained by employing collectors such as potassium amyl xanthate. Again selective flocculation of synthetic mixtures was more successful than natural ones. Three combinations of minerals were successfully

separated; crysocolla and quartz, malachite and quartz and malachite, calcite and dolomite.

Yarar and Kitchener (33) carried out extensive testwork on quartz, galena and calcite. They found that with favourable mixtures such as quartz and galena, high grades and recoveries were obtainable in one or more stages. However, in other systems, such as calcite and galena, mutual coagulation occurred and as such it became necessary to incorporate modifying agents (dispex and sodium sulphide).

Preconcentration, by the selective desliming of quartz gangue from pyrite, galena, sphalerite and smithsonite, using flocculants, has been reported by Usoni et al (70). They also noted that for the latter two minerals, flotation recoveries could be improved by up to 40% utilising this method.

Attia and Kitchener (39) have prepared and tested a number of water soluble polymers containing groups which chelate or complex with heavy metal ions. Evidence for selectivity has been achieved for synthetic mixtures of finely divided minerals. One such polymer, PAMG, (polyacrylamide glyoxal-bis-(2 hydroxyanil)) has been used successfully in the laboratory, for the upgrading of a typical oxidised copper ore of Zaire. Similarly Srestry and Somasundaran (93) have successfully separated haematite from quartz using sodium polystyrenesulphonate and causticised corn starch, and chalcopyrite from quartz using a xanthated polymer. These studies demonstrate the usefulness of functional groups in selective flocculation.

On a similar line, selective chelating groups have also been introduced into dispersants. Catechol and phenol were incorporated into dispex N40 and proved to be a selective dispersant for calcite dolomite and fluorite (69), whilst xanthated dispersants, having affinity towards pyrite, but not towards coal, have been successfully applied in the selective flocculation of coal from pyrite (95).

The selective flocculation of colloidal phosphate ore from clays was patented by Haseman in 1951 (96) and incorporated sodium hydroxide as a dispersant and starch as the flocculant. Davenport et al (97) made use of a similar reagent system to design a continuous process for the beneficiation of hard rock phosphate. However, they concluded that the high cost of dewatering the concentrate, together with its relatively high R_2O_3 content, would impose serious economic constraints.

A method of purifying kaolin clay containing titania impurities has been patented by Mercade (98). Addition of polyvalent cations, such as calcium chloride, followed by an anionic polyacrylamide, resulted in the formation of titania flocs; these were easily separable from the unflocculated portion.

Brogotti et al (99) have patented a process which allows the desliming of sylvinite ores by selective flocculation, followed by the removal of slimes by froth flotation. This involves treatment of the ore pulp with a high molecular weight non-ionic polyacrylamide to flocculate the slimes, which are then further treated with a cationic collector and subjected to froth flotation. This process,

it is claimed, can reduce the loss of sylvinite values from between 10 - 15% to less than 1%.

A number of authors have studied the selective flocculation of coal/shale slurries and all but one (67) have noted that coal is the flocculated component, regardless of coal/shale ratios.

Hucko (100) in his study on coal beneficiation, evaluated numerous flocculants and dispersants, at various pH values and ionic concentrations. Test work showed that a low molecular weight non-ionic flocculant, in conjunction with a large dosage (several lbs/ton) of one of many effective dispersants, sodium hexametaphosphate, sodium tripolyphosphate or sodium carboxymethylcellulose, resulted in a good separation. Highly alkaline conditions also favoured this system, except when sodium carboxymethylcellulose was used as a dispersant. An effective two product separation however was not achieved, with the coal fraction giving a high ash product requiring further cleaning stages; this was as a result of shale entrainment.

Latex has been found to be a useful material for the removal of clay sludge from coal slurries prior to flotation (101). Commercial plant trials using this material, have been undertaken with the intention of entirely replacing flotation by a selective flocculation process. The conclusions drawn from the study were that, whilst selective coal slurry flocculation using latex was an effective cleaning process, the quality of the cleaned product was slightly lower than that obtained by flotation.

Separation of coal from shale has been achieved at high pH using Purifloc A22 (a high molecular weight anionic polyacrylamide). In the same study (95) the separation of pyrite from coal, using a specially developed dispersant,was found to be effective and as such, the selective flocculation of coal from pyrite and shale was possible by a combination of these two reagents.

Using tetrasodium pyrophosphate and a calcium salt as dispersants,in conjunction with a polyacrylamide flocculant, effective separation of coal/shale mixtures has also been achieved by Blagov (102).

Only one author has claimed selective flocculation of the shale component (67). This was accomplished with the use of sodium carboxymethylcellulose (as a dispersant) and "Gigtar", a modified anionic polyacrylamide, (as a flocculant). However, although suspension ash contents were low at 4 - 10%, very little coal remained in suspension (generally less than 15%) and the ash contents of the sediments were only increased by about 10% over the starting point.

To summarise, it is concluded that although many workers have successfully achieved selective flocculation, there would appear to be no set procedure which may be applied in advance to determine which will be the most effective polymer for a particular mineral mixture. However, what has become clear is that good dispersion of one component is essential for efficient selective flocculation and that selective dispersants have achieved considerable success in

this area. . Other methods which have been effective in achieving enhanced polymer adsorption are pH variation and pretreatment of one mineral specie. Specially prepared chelating polymers have also proved to be fruitful, however many experimental avenues have yet to be explored before the subject is fully understood.

What has become clear in this chapter is that selective flocculation may be approached using two polymer types; commercially available and modified. Within the Mining Engineering Department at Nottingham University both avenues have been explored; this project is concerned only with the use of the former, in conjunction with an alkali polyphosphate as dispersant.

CHAPTER 3

SELECTION AND PREPARATION OF COAL, SHALE AND POLYMER SAMPLES

3.1 COAL AND SHALE SAMPLES

Since the ultimate aim of the project was to explore the possible use of selective flocculation for the separation of fine coal/shale mixtures, 63 μm was taken as the upper size limit for experimental work.

It was decided to select one material only, that from Bentinck Colliery, which is located in the South Nottinghamshire Area, and obtain bulk samples of pure coal and shale, to be used in all experimental work. This, it was felt, was the only way to obtain a supply of material with constant characteristics. Thus any variations in results obtained would then be ascribable, as far as possible, to the particular experimental conditions, rather than a change in coal or shale properties. Such treatment does not duplicate actual plant conditions, but represents ideal circumstances under which the surface properties of the coal and shale particles remain unaltered; thus their amenability to selective flocculation is most likely to be revealed. To ensure that the coal and shale obtained for the tests was free from any chemical additives samples were taken after gravity separation. About 200 kg of +50 mm coal and shale was sampled and transported to the Mining Department. All the coal and shale was then washed, to remove any fines adhering to it and left to air dry for about four days. Both samples were treated in the same manner.

A Sturtevant jaw crusher was employed initially to crush the samples to -1.4 mm, followed by grinding in a vibration mill. A Russell Finex Screen, at 63 μm, was used to sieve the material, with any oversize being returned to the vibration mill for regrinding. Each complete sample was then carefully mixed and riffled, in stages, until sub-samples of approximately 1½ kg were obtained. These were then placed in plastic bags and sealed until required.

An X-ray fluorescence scan of the shale indicated its main constituents to be kaolinite, illite and quartz.

Three bags of coal and three of shale were then chosen at random, in order that size and ash analyses could be performed to examine the representability of each sample as a proportion of the whole.

3.1.1 Size Analysis

The size analysis was carried out using the Coulter Counter Model D Industrial, as illustrated in Plate 1 (103).

Size analyses obtained for the three sub-samples are shown in Tables 3.1 and 3.2 with the average size analyses presented graphically in Fig. 3.1. Actual Coulter Counter data sheets are given in Appendix 1.

It may be assumed, therefore, that any bag taken from those prepared will be representative of the whole sample, with regard to size analysis.

PLATE 1


STIRRER
MANOMETER
THRESHOLD (T)
SENSITIVITY CONTROLS
OFF
ATTENUATION
APERTURE CURRENT
0-066
0-033
0-017
0-0083
0-0053
0-0033
0-130
0-25
0-5
PYREX
200
150
100
COULTER COUNTER
COULTER ELECTRONICS LTD HARPENDEN HERTS ENGLAND
INDUSTRIAL D

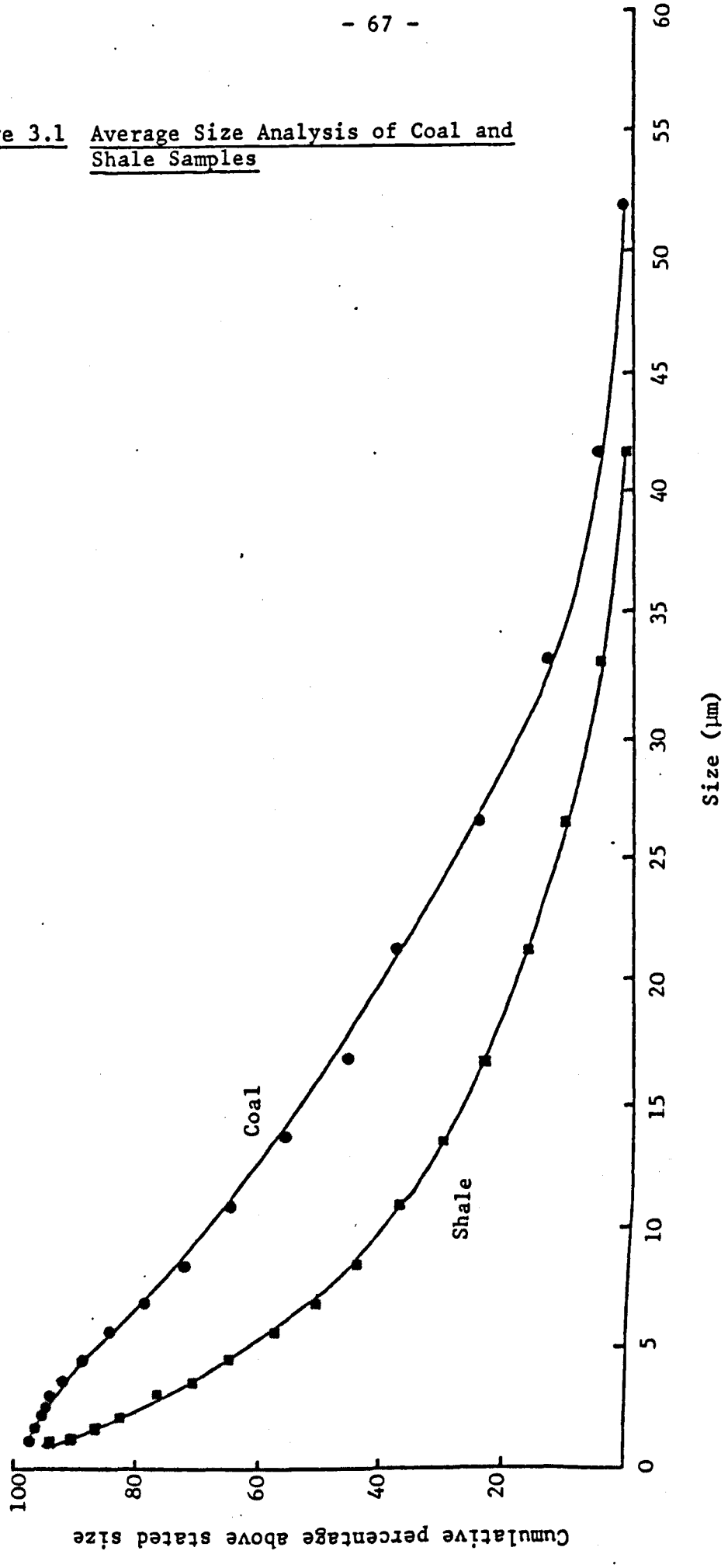
Table 3.1 Size analyses of Shale

	Cumulative weight percentage above stated size			
μm	Sample (1)	Sample (2)	Sample (3)	Average
41.6	-	1.12	2.25	1.6
33.0	4.23	4.48	8.82	5.6
26.5	10.2	11.3	12.4	11.3
21.2	15.3	16.9	18.6	16.9
16.8	21.0	24.3	26.0	23.8
13.5	29.4	30.2	32.1	30.5
10.7	37.4	37.2	39.2	37.9
8.48	44.3	43.3	44.9	44.2
6.73	52.2	48.9	51.1	50.8
5.51	58.0	56.4	58.5	57.6
4.56	65.1	63.3	65.3	64.6
3.62	70.3	69.3	72.2	70.6
3.09	76.9	75.6	78.3	76.9
2.19	81.3	81.2	84.2	82.2
1.81	85.5	85.7	87.8	86.3
1.44	90.0	90.6	93.2	91.3
1.23	92.9	93.5	95.8	94.1

Table 3.2 Size analyses of Coal

	Cumulative weight percentage above stated size			
μm	Sample (1)	Sample (2)	Sample (3)	Average
54.4	0.77	1.3	-	1.0
41.6	5.48	8.2	4.09	5.9
33.0	15.4	12.6	14.1	14.0
26.5	26.0	24.8	25.7	25.5
21.2	37.7	36.8	39.8	38.1
16.8	45.7	46.0	47.3	46.3
13.5	56.4	54.6	57.6	56.2
10.7	64.9	64.0	66.5	65.1
8.48	72.5	71.2	73.8	72.5
6.73	79.5	76.9	79.9	78.8
5.51	85.0	82.0	85.4	84.1
4.56	89.6	86.5	89.5	88.6
3.62	93.0	90.3	92.9	92.1
3.09	95.5	93.1	95.3	94.6
2.67	95.8	-	95.6	95.7
2.19	97.1	96.1	96.9	96.7
1.81	97.9	97.4	97.9	97.7
1.44	98.5	98.6	98.7	98.6
1.23	98.9	99.1	99.1	99.0

Figure 3.1 Average Size Analysis of Coal and Shale Samples



3.1.2 Ash Analysis

Since the ash content of the products obtained from the selective flocculation process were to provide guidelines regarding the effectiveness of the process, it was necessary to determine the initial ash content of both coal and shale.

Ash analyses were carried out according to BS 1016, (104) on part of the same three sub-samples used for size analysis. The results are given in Tables 3.3 and 3.4.

Sub-sample	Wt. % Ash	Average wt. % Ash
1	4.75, 4.85, 4.63	4.74
2	4.64, 4.68, 4.73	4.68
3	4.62, 4.70, 4.72	4.68
	Overall Average =	4.70%

Table 3.3 Ash analyses of coal

Sub-sample	Wt. % Ash	Average wt. % Ash
1	87.48, 87.34, 87.49	87.44
2	87.30, 87.24, 87.06	87.20
3	87.22, 87.30, 87.27	87.26
	Overall Average =	87.30%

Table 3.4 Ash analyses of shale

Again, with regard to ash analysis, it may be assumed that any bag will be a representative sample of the whole and that a 50/50 w/w mixture (to be used in selective flocculation testwork) will have an average ash content of 46%.

3.2 INITIAL POLYMER SAMPLES

Since the aim of the project was to determine the suitability of commercially available flocculants, in conjunction with a dispersant, for the treatment of fine coal/shale systems, a total of twenty seven polyacrylamide flocculant samples were initially obtained, from two manufacturers. These had a wide range of molecular weights and ionic characters and for the purpose of the study, were divided into two groups according to their molecular weights. Tables 3.5, 3.6 and 3.7 indicate both the molecular weights and ionic characters of each of the flocculants obtained.

3.2.1 Polymer Preparation

Throughout the testwork, polymer solutions of 0.05% w/v were used, as it had already been established that dilute solutions allowed more thorough mixing of the flocculant with the slurry (28). These were prepared using the following procedure: 0.25 g of polymer powder was weighed into a dry 500 ml volumetric flask and 'wetted' with approximately 3 ml of methanol. Distilled water was then added, to volume, and the whole shaken vigorously for about 30 secs, then left to stand, with occasional shaking, for between 3 - 4 hrs, to ensure complete dissolution. Polymer solutions were stored for 24 hrs only, after which time they were discarded and fresh solutions prepared.

Polymer Identification	Molecular Weight	% Ionic Character
A6	20×10^6	50 Anionic
A5	17×10^6	40 Anionic
A4	23×10^6	30 Anionic
A3	18×10^6	20 Anionic
A2	13×10^6	10 Anionic
A1	23×10^6	5 Anionic
NI	18×10^6	Non-Ionic
C1	16×10^6	5 Cationic
C2	14×10^6	10 Cationic
C3	14×10^6	30 Cationic
C4	9×10^6	70 Cationic

Table 3.5 High molecular weight polymers (Manufacturer X)

Polymer Identification	Molecular Weight	% Ionic Character
A10	8×10^6	100 Anionic
A9	9×10^6	75 Anionic
A8	12×10^6	50 Anionic
A7	9×10^6	10 Anionic
C5	10×10^6	10 Cationic
C6	6×10^6	30 Cationic
C7	9×10^6	50 Cationic
C8	6×10^6	80 Cationic

Table 3.6 Medium molecular weight polymers (Manufacturer X)

Polymer Identification	Molecular Weight	% Ionic Character
S	High	Non-Ionic
T	High	Non-Ionic
U	High	5 Anionic
V	High	10 Anionic
W	High	15 Anionic
X	High	20 Anionic
Y	High	30 Anionic
Z	High	35 Anionic

Table 3.7 High molecular weight polymers (Manufacturer Y)

CHAPTER 4

EXPERIMENTAL WORK ON INITIAL POLYMER SAMPLES

4.1 SETTLING VELOCITIES

The object of the initial testwork was to determine which of the polymers were the most effective in producing flocculation of separate coal and shale samples. In order to establish this, simple settling rate tests were conducted, with each of the polymers; these were also combined with a visual appraisal of the supernatant clarity.

It has been established that dispersion of one or both components of a mixed slurry was necessary for selective flocculation, and it was considered that, when, at a later point, mixed systems were to be tested for selective flocculation, the addition of a dispersant would be essential. In order to be meaningful basic settling tests should be performed under similar conditions. A major component of the shale was kaolinite, which at low to neutral pH exhibits negative faces and positive edges and thus possesses a certain degree of natural coagulation (51). Alkali polyphosphates have been widely used in the dispersal of a variety of suspensions (105, 106) and more recently in a study on coal beneficiation (100). The interaction of such polyphosphates with kaolinite has been studied by Michaels (107), who proposed four mechanisms for the dispersion behaviour:

1) replacement of polyvalent cations by monovalent cations in the diffuse double layer associated with the platelet faces.

2) elimination (via polyanion retention in the double layer) of positively charged edges sites.

3) adsorption of anions at the platelet faces.

4) adsorption of anions at the platelet edges in excess of the number of cationic sites usually present.

Proposal (4) was thought to be the most likely since it produces a particle having all parts of its surface negatively charged and thus creates interparticle repulsions at all possible configurational positions; experimental work tended to confirm this view. On the basis of the above, Calgon (sodium hexametaphosphate) was selected. A concentration of 0.08 kg/tonne was used, since initial tests showed that this was the minimum dosage required to retain a 5% w/v solids shale slurry in suspension over a period of 24 hours.

A solids concentration of 5% w/v was maintained throughout; this is comparable with both a typical flotation feed and the cyclone overflow of a coal preparation plant. On the basis of advice from the local water authority, calcium (0.1 kg/tonne) and magnesium (0.09 kg/tonne) ions were also added to distilled water in order to simulate plant water conditions.

4:1.1 Experimental

Fifty grams of coal or shale were taken and added to 1 litre of distilled water containing calgon (0.08 kg/tonne), Ca^{2+} (0.1 kg/tonne) and Mg^{2+} (0.09 kg/tonne). This was mixed at 3,500 r.p.m. for 2 minutes. The stirrer speed was reduced to 450 r.p.m. and the required dosage of polymer added (0.05%) over a period of approximately 1 minute; once polymer addition was complete stirring was discontinued.

The flocculated slurry was immediately poured into a cylinder and the time taken for the mineral/water interface to fall a set distance. A visual assessment of the supernatant clarity was also made. Polymer dosages of between 0.025 and 0.30 kg/tonne were used. The pH of the dispersed slurry was recorded at 6 - 6.5 throughout.

The results of all of the tests are given in Appendix 2 and typical results are presented graphically in Figures 4.1 to 4.8.

4.1.2 Observations and Discussion of Settling Tests

Using cationic polymers (Figures 4.1 and 4.2) the supernatant clarities of flocculated coal slurries were generally superior to those of shale when considerable quantities of solids remained in suspension. With anionic polymers however, (Figures 4.3 and 4.4) supernatant clarities of both coal and shale were more comparable. Improvements in the clarities of anionically flocculated coal and shale slurries were noted with increasing polymer molecular weight. However, with cationic polymers, only the clarity of the coal slurries was improved with an increase in molecular weight.

In the following discussion, due to the considerable quantities of solid remaining in suspension, settling velocities of less than 1.2×10^{-3} ms^{-1} for shale are regarded as poor, i.e. little flocculation actually occurred. On the other hand for coal, similar settling velocities produced a greater settled mass and thus clearer supernatant, these were therefore regarded as being significant.

For the purposes of this discussion, it is assumed that both the coal and shale were negatively charged (108) at the chosen pH

Figure 4.1 Variation of Settling Rate with Polymer Dosage - Cationic Medium Molecular Weight Polymers

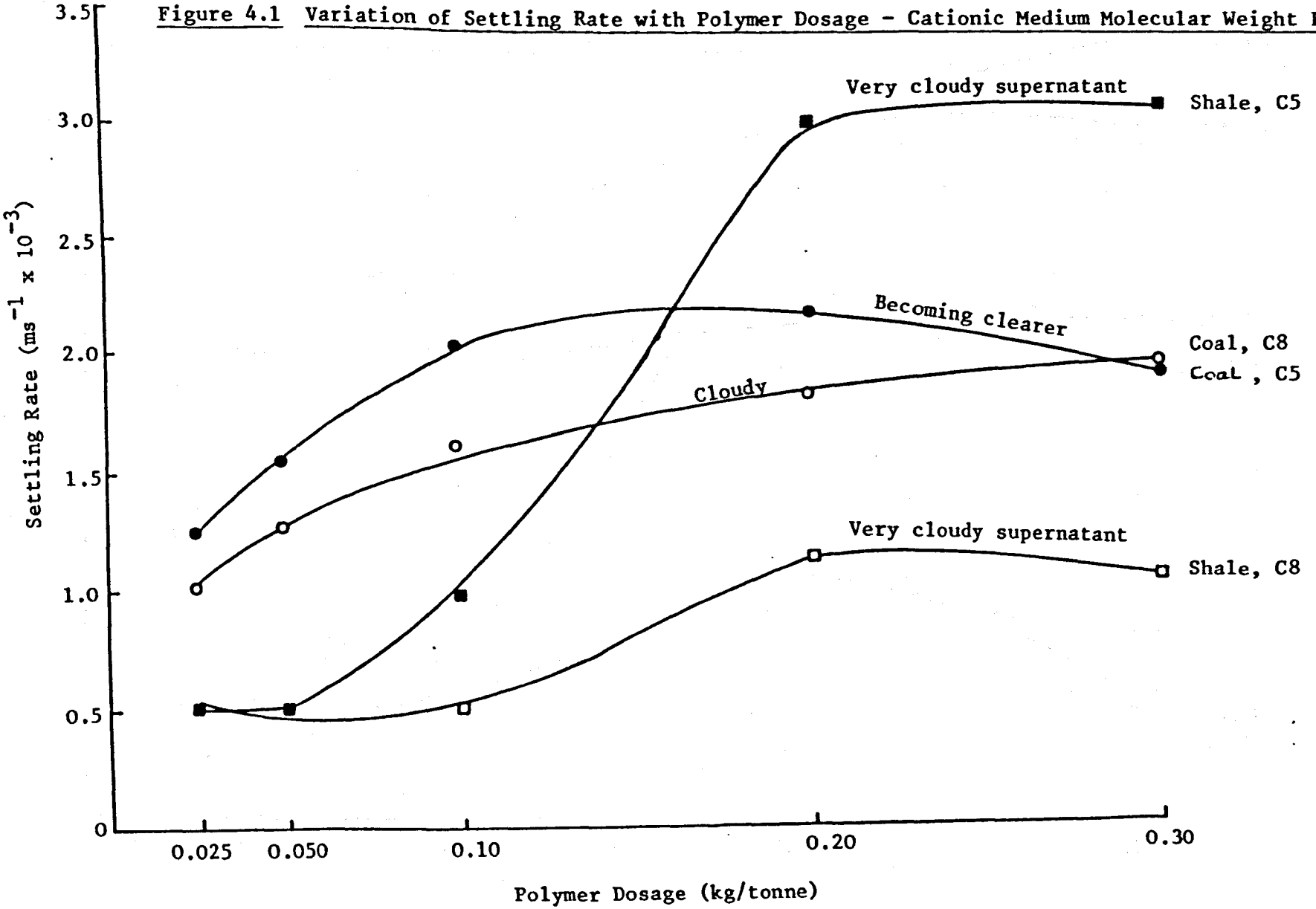


Figure 4.2 Variation of Settling Rate with Polymer Dosage - Cationic High Molecular Weight Polymers

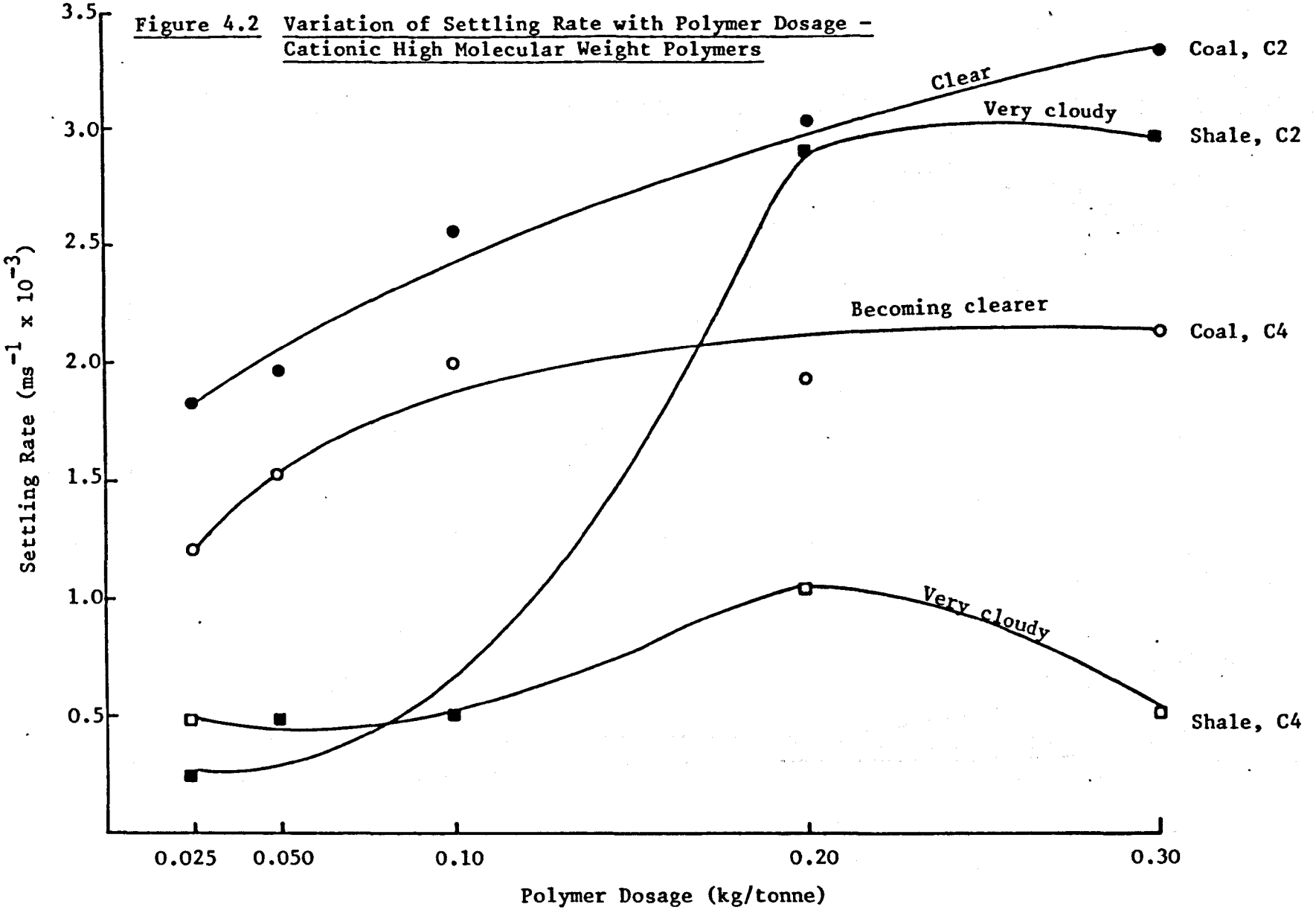


Figure 4.3 Variation of Settling Rate with Polymer Dosage - Anionic Medium Molecular Weight Polymers

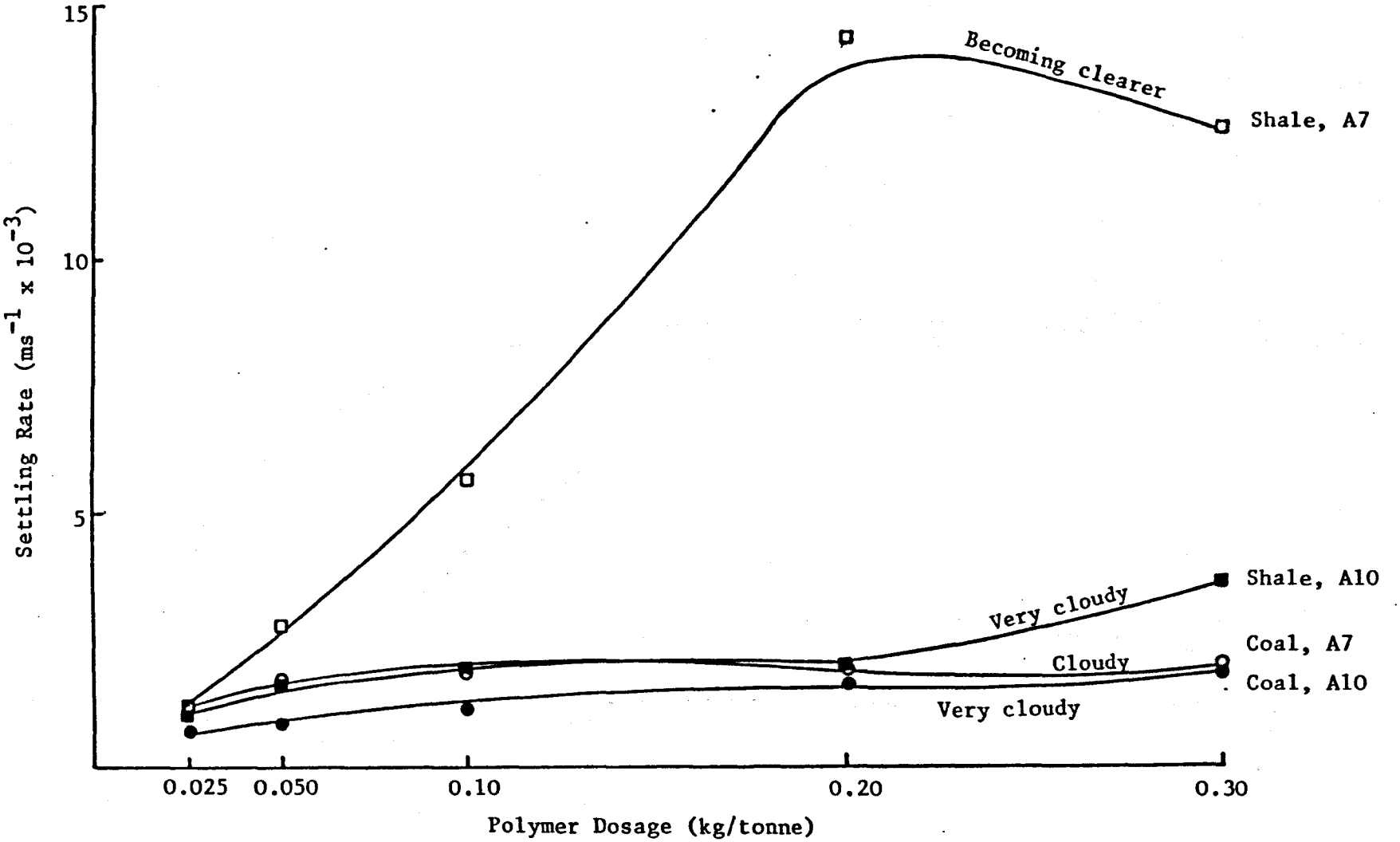
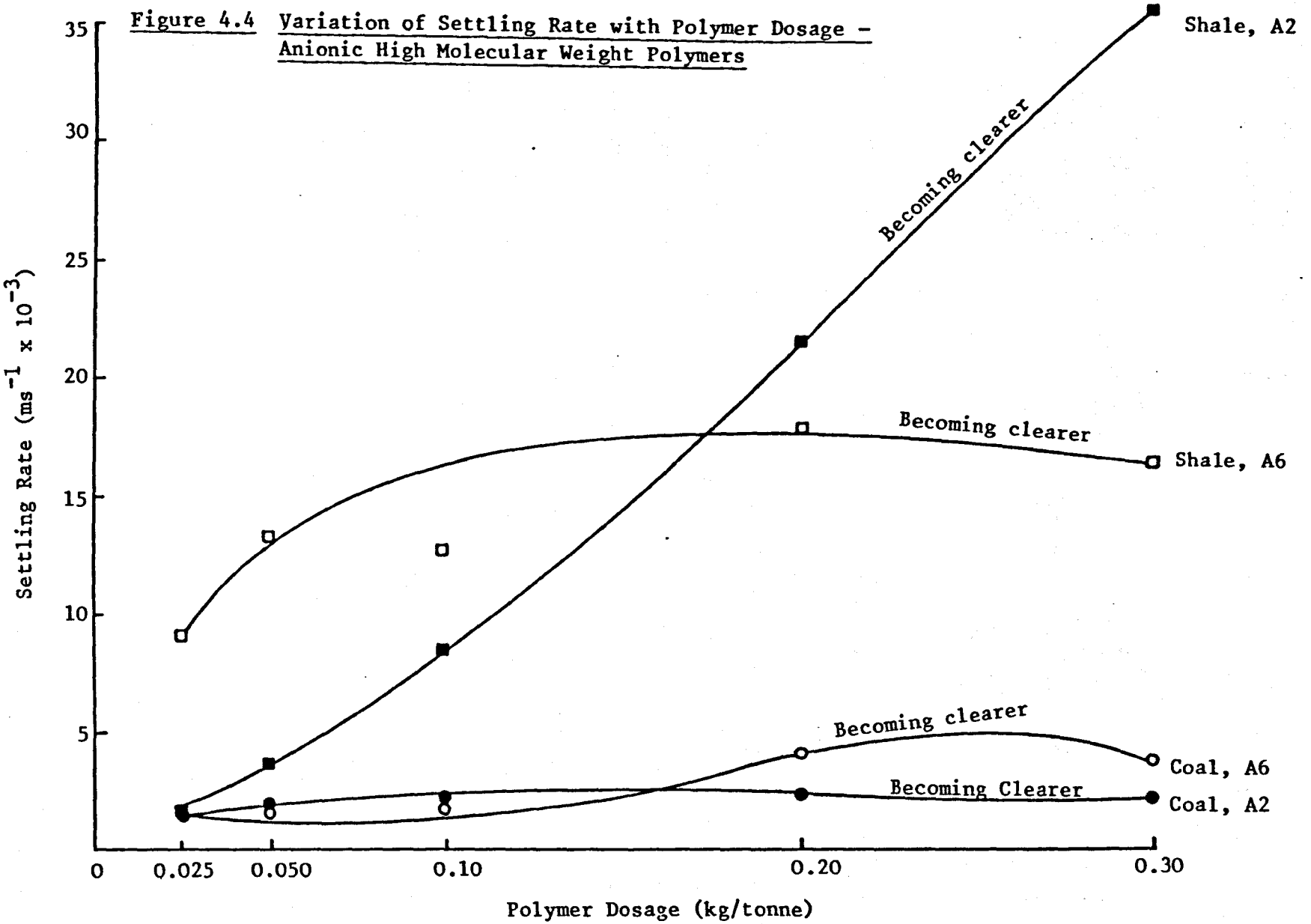


Figure 4.4 Variation of Settling Rate with Polymer Dosage - Anionic High Molecular Weight Polymers

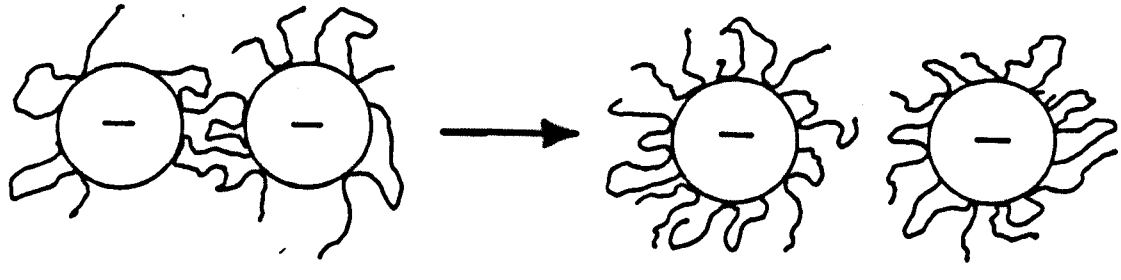


and that the mechanism of flocculation was that of bridging (section 2.1.2.2); the latter was assumed on the basis of its wide acceptance (see also section 4.1.3).

Without polymer addition, the settling velocities of coal and shale were 0.3 and 0.35 $ms^{-1} \times 10^{-3}$ respectively.

From Figures 4.1 to 4.4 several observations can be made, the most fundamental being the effect of increased dosage on the settling velocities of both coal and shale. Despite the presence of calgon it is apparent that, in most cases, an increase in polymer dosage resulted in an increase in settling velocity, after which it either levelled out, or, in some cases, fell. The latter being due to a lack of available surface sites for bridging. This situation is shown diagrammatically in Figure 4.9. Furthermore from Figures 4.1 and 4.2 (cationic polymers) it can be seen that, in general, the settling velocities of coal were higher than those of shale, whereas in Figures 4.3 and 4.4 (anionic polymers) the reverse is

Figure 4.9 Restabilisation of Particles with Excess Polymer Dosage



1. Particles flocculated

2. Particles restabilised - unable to bridge due to lack of available surface sites.

true. It is suggested that this is due to different modes of adsorption of the two polymer types onto the individual coal and shale surfaces. One non-ionic polymer, of high molecular weight was also tested and found to produce similar settling velocities for both coal and shale.

Considering the graphs in more detail, Figure 4.1 shows the effect on the settling velocities of coal and shale, when employing a 10% and an 80% medium molecular weight cationic polymer. These are referred to as C5 and C8 respectively. Both produced similar settling velocities for coal, but for shale the results were quite different, with C5 producing the higher rates in the majority of cases. This probably relates to the effect of the high cationic character of C8 which, due to electrostatic attraction, may have increased its adsorption at the negatively charged shale surface, leaving few "loops and tails" available for flocculation by bridging. On the other hand, since polymer C5 has a much lower percentage cationic character, the strength of adsorption may be reduced at the shale surface, hence providing improved bridging conditions. For coal, when employing either C5 or C8, settling velocities and resultant supernatant clarities were more acceptable. This may be the result of the lower negative zeta potential of coal (108) and its influence on polymer adsorption; reduced electrostatic attraction between the coal and polymer molecule is likely to occur. As such, cationic polymer chains remain sufficiently extended into solution in "loops and tails" for bridging to occur. It would therefore appear that both the polymer dosage and its percentage cationic character exerted a greater influence on the settling velocities of shale than on those of coal.

The polymers utilised in Figure 4.2 are of similar cationic characters to those in Figure 4.1, but have higher molecular weights. Due possibly to the overriding influence of positive charge density, this factor has negligible effect on shale settling velocities. However for coal, due to the formation of larger flocs, some increase in settling velocity is noted.

Figure 4.3 shows the variations in settling velocities using a 10% and a 100% medium molecular weight anionic polymer, referred to as A7 and A10 respectively. Here it is evident that A7 was the most effective for shale flocculation with A10 apparently being less suitable. Two factors were believed to be in competition (8a). The first being that as charged group density increases, chain extension and bridging are favoured producing large flocs. Secondly, however, is the fact that at 100% anionic character, due to increased electrostatic repulsion with the similarly charged shale surface, adsorption of the flocculant is hindered. For coal, the 10% anionic polymer also proved to be a more effective flocculant, producing somewhat higher settling velocities. However with A10, possibly due to the lower coal zeta potential (108), reductions in flocculating ability were not as marked as in the case of shale.

Figure 4.4 shows the effect of a reduction in anionic character to 50% (A6), on the settling rates of shale. Reduced electrostatic repulsions resulted in more effective polymer adsorption and thus more efficient flocculation. Polymer A2 (10% anionic) produced very high settling rates for shale at high dosages, but it cannot be stated with any certainty whether this was the result of changes in molecular weight, ionic character or dosage, or indeed a combined

effect of all three. For coal, settling velocities at low polymer dosages were highest using the polymer having the lower anionic character, with the reverse occurring at higher dosages. Due to the variation in the molecular weights of the two polymers concerned, it is difficult at this stage to explain why this occurred, since this factor may have masked any others which were in operation Comparing polymers A7 and A2 in Figures 4.3 and 4.4 : the settling rates for both coal and shale were, as expected, considerably increased when employing the higher molecular weight product.

Figures 4.5 to 4.8 attempt to show the effect of ionic character on the settling rates. This proved very difficult due to the fact that each set of polymers comprised a group with a wide molecular weight spread. However, the main, general points observed are discussed below.

In Figure 4.5, at low polymer dosage, a maximum for shale occurred at 50% anionic character; this corresponds with the polymer having the highest molecular weight in this group, and is presumably due to the formation of larger flocs. In Figure 4.6, however, at higher dosages,this maximum is displaced to 10% anionic character. This may be a result of changes in any of the three variables, molecular weight, anionic character or dosage. In contrast settling velocities of coal varied little and as such appeared to be less dependent upon molecular weight, when this was below 12×10^6.

Figure 4.7 shows similar trends to Figure 4.5 in that the two settling rate maxima for shale correspond to the highest molecular weight polymers. Again however, on increasing the polymer dosage,

Figure 4.5 Variation of Settling Rate with Polymer Ionic Character - Medium Molecular Weight (0.025 kg/tonne)

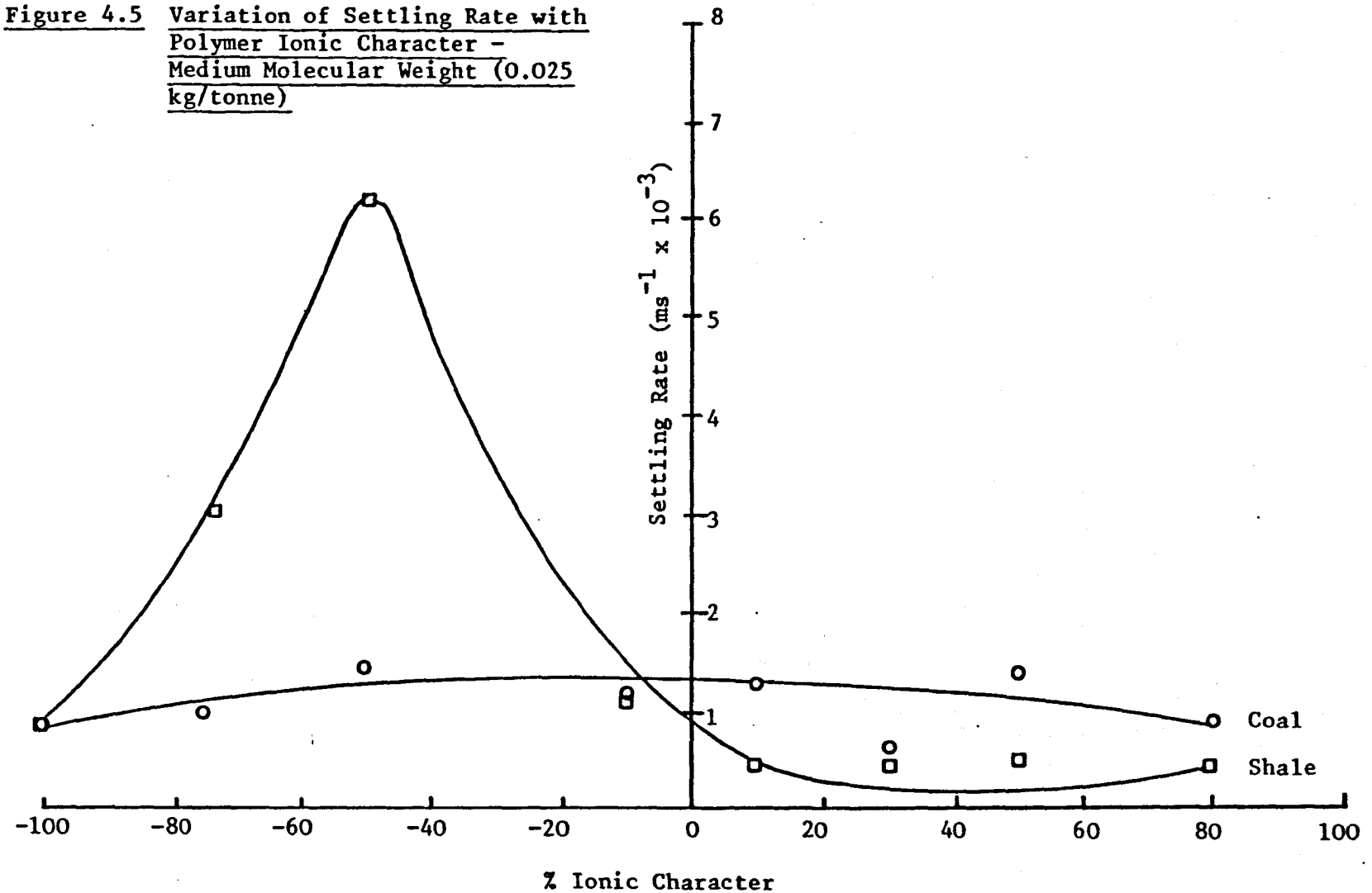
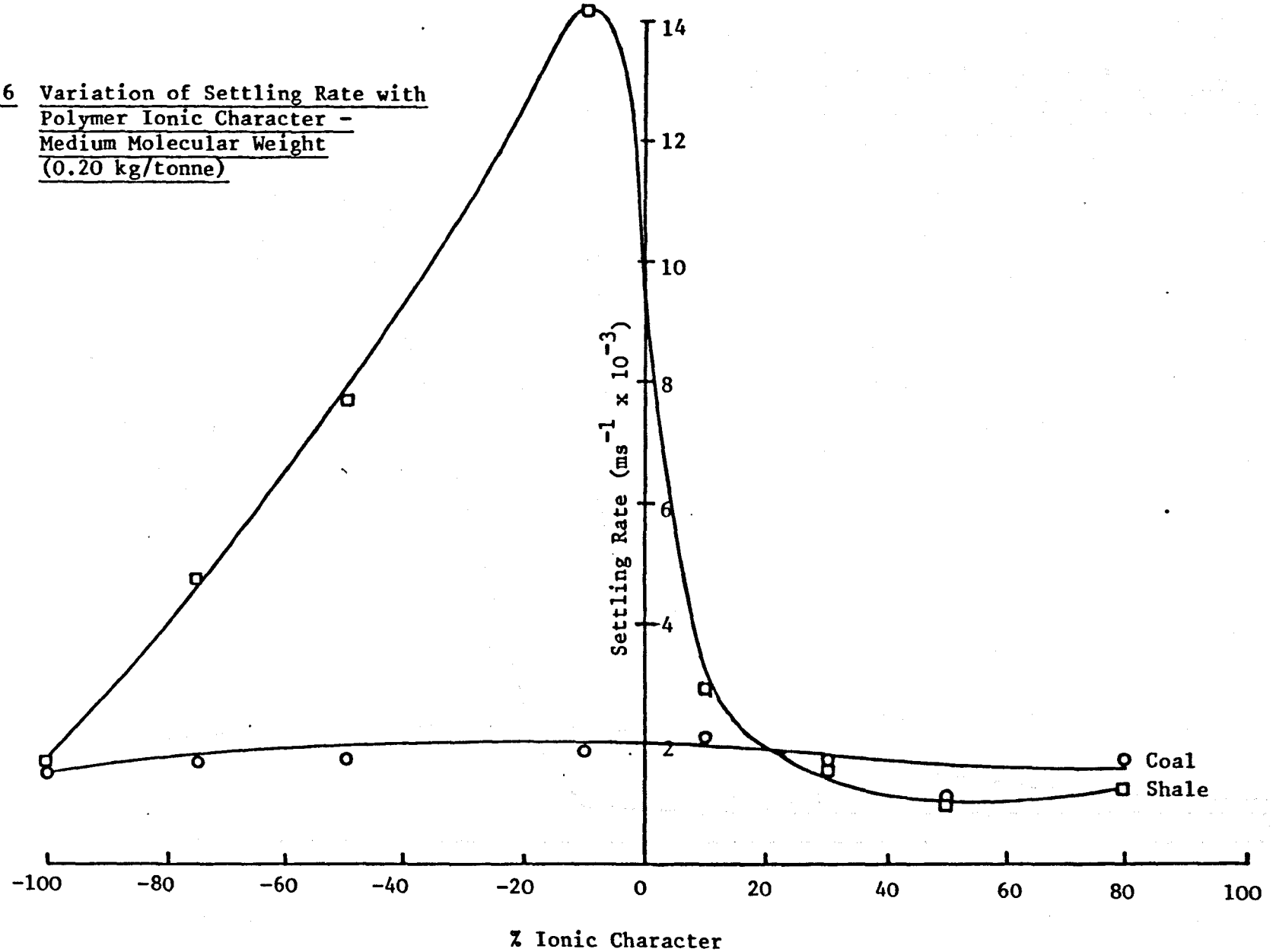


Figure 4.6 Variation of Settling Rate with Polymer Ionic Character - Medium Molecular Weight (0.20 kg/tonne)



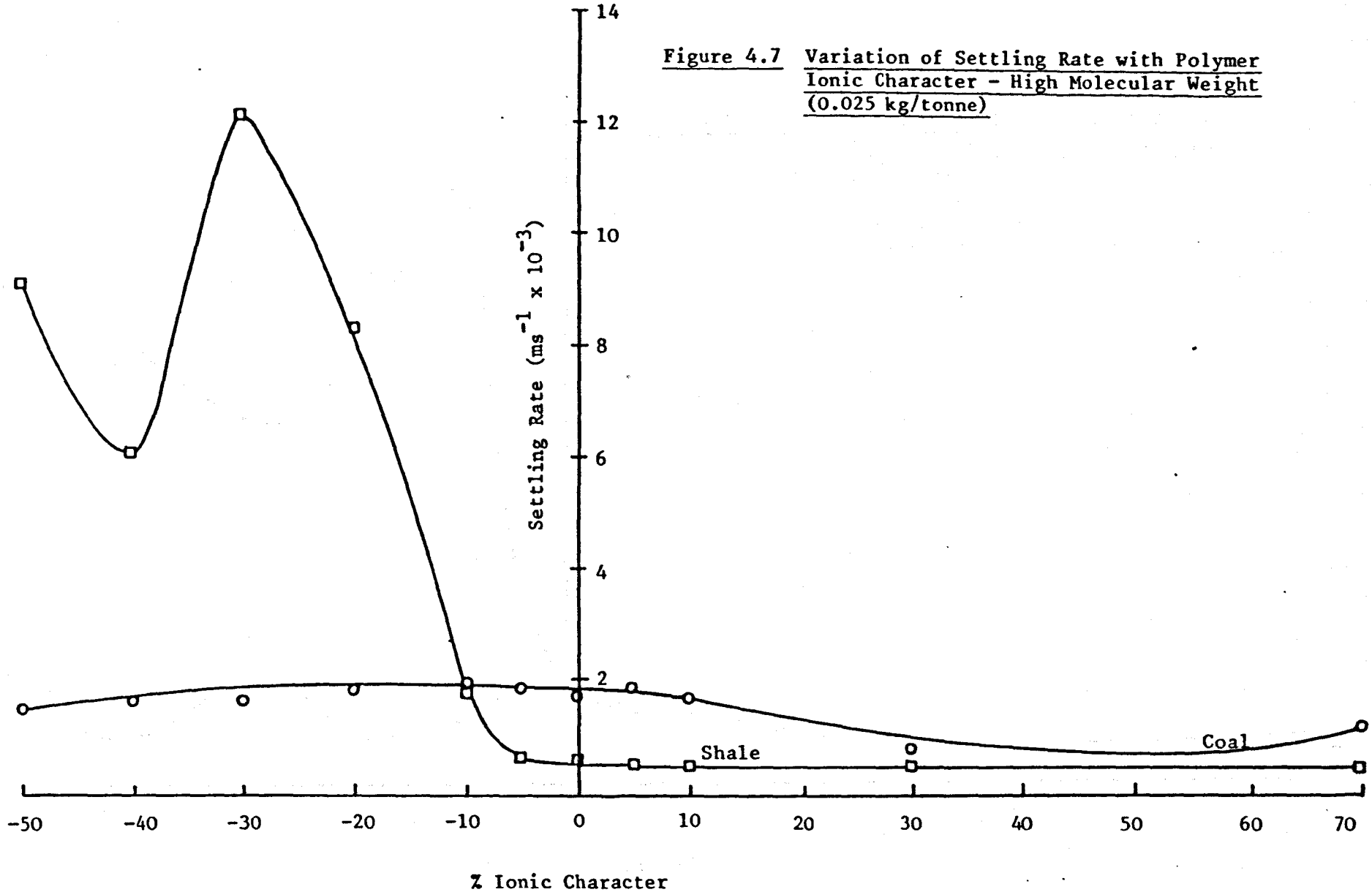


Figure 4.7 Variation of Settling Rate with Polymer Ionic Character - High Molecular Weight (0.025 kg/tonne)

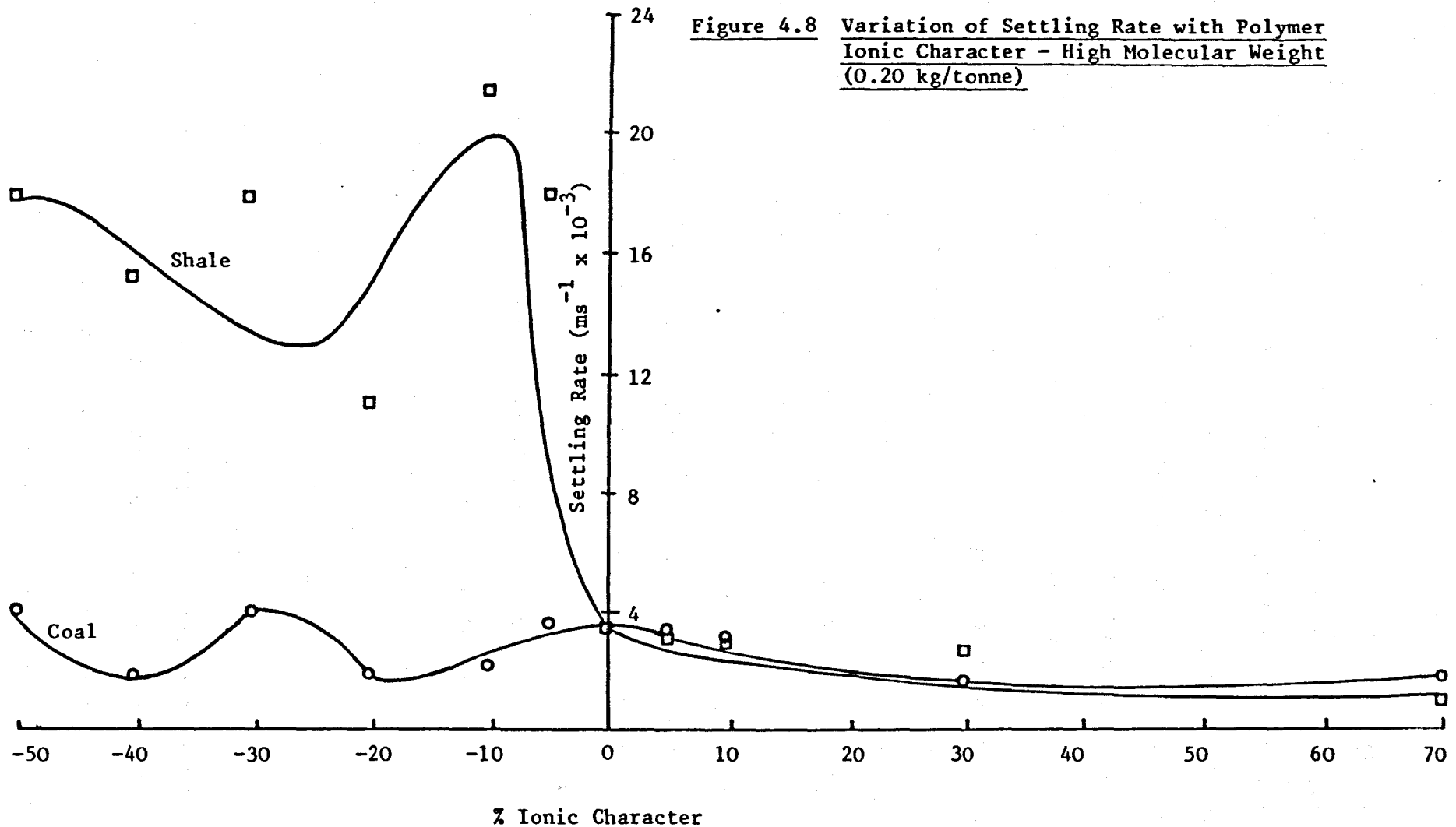


Figure 4.8 Variation of Settling Rate with Polymer Ionic Character - High Molecular Weight (0.20 kg/tonne)

as seen in Figure 4.8, these maxima change position. An explanation for this is again not possible. Here the settling rates of coal also appeared to be affected by molecular weight, with increased settling velocities occurring at 50% and 30% anionic character. Hence it would appear that, for shale slurries at low polymer dosage, molecular weight increases lead to higher settling rates. However, for coal, settling velocities are only increased using polymers with a molecular weight exceeding approximately 12×10^6 and at a high dosage.

Five main points thus emerge from studying the settling velocities of coal and shale slurries.

1. All flocculants increased the settling rates of both coal and shale to various degrees.

2. Maximum variations in settling rates were obtained with shale.

3. The settling rate of shale with cationic polymers was generally lower than that for coal and decreased with an increase in cationic character.

4. Anionic flocculants greatly increased the settling rates of shale, reaching a maximum of 36×10^{-3} ms^{-1} these being dependent, to some extent, upon anionic character, molecular weight and dosage.

5. The settling rate of coal was also dependent upon dosage, ionic character and molecular weight.

Due to large variations in the molecular weights and ionic character of the polymers points 4 and 5 cannot, at this stage, be enlarged further. Polymers obtained from the Manufacturer Y were also tested and produced good settling velocities. However, due to the fact that their molecular weights were unknown, results obtained have not been discussed. They are however included in Appendix 2(e) and 2(f).

4.1.3 Proposed Mechanisms of Polymer Adsorption

It is clear from the previous discussion that, in spite of the addition of calgon, most anionic polymers, were suitable for the flocculation of shale, with the exception of the 100% anionic polymer. This may be considered to be unusual since it might be expected that electrostatic repulsions between the two similarly charged materials would prevent adsorption; hence the mechanisms involved in bonding must have overcome the repulsive forces. To account for the flocculation of clays by anionic polyelectrolytes, Michaels and Morelos (109) suggested the following:

(1) A hydrogen bonding mechanism between unionised carboxyl and amide groups of the polymer and oxygen atoms on the solid surface, as seen in Figure 4.10.

(2) Formation of electrostatic bridges - polyvalent cations such as Ca^{2+}, which are usually present in clays, may act as an electrostatic bridge. This is shown diagrammatically in Figure 4.11.

(3) Anion interchange, in which carboxylate ions replace adsorbed anions, such as hydroxyl, on the clay surface.

In an attempt to clarify the mechanisms they examined the adsorption of sodium polyacrylate and partially caustic-hydrolysed polyacrylamide on purified hydrogen kaolinite (i.e. polyvalent cation free) at various pH levels. The theory behind the investigation was that if mechanism (1) was occurring then the reaction

$$\text{Clay-OH} + \text{HOOCR} \rightleftharpoons \text{ClayO}\overset{\text{H}}{\underset{\text{H}}{\text{H}}}\text{OOCR} \rightleftharpoons \text{ClayO}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R} + \text{H}_2\text{O}$$

would be favoured by a high concentration of unionised carboxylate i.e. adsorption of polymer would decrease with increasing pH. On the

Figure 4.10 Hydrogen Bonding Mechanisms

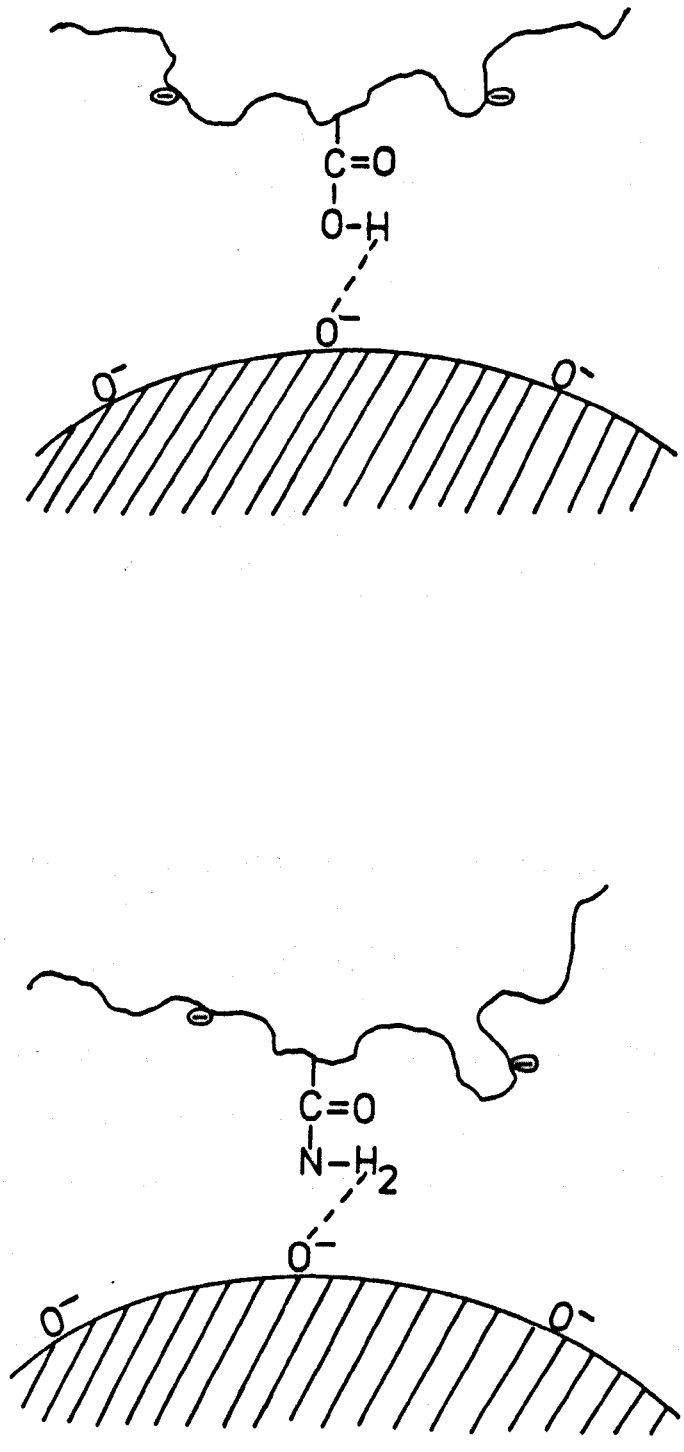
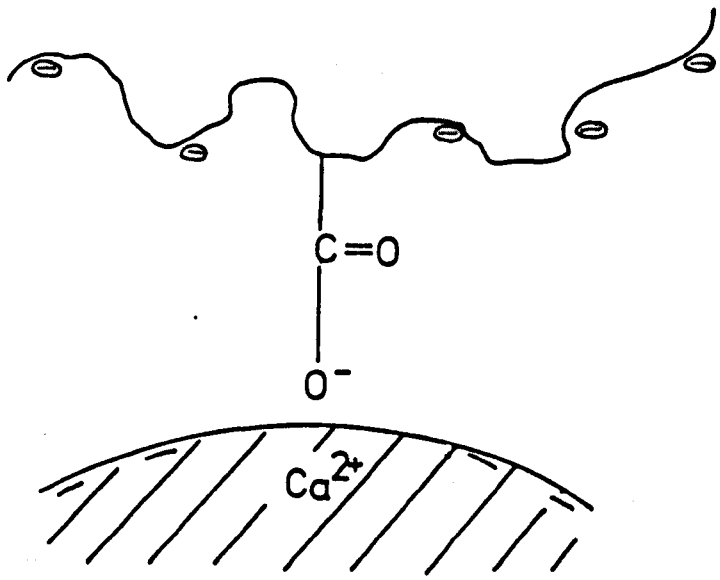


Figure 4.11 Electrostatic Bridge Formation



other hand if mechanism (3) was correct then the reaction

$$Clay^{+}\text{-}A^{-} + RCOO^{-}H^{+} \rightleftharpoons Clay^{+}\text{-}OOCR + M^{+}A^{-}$$

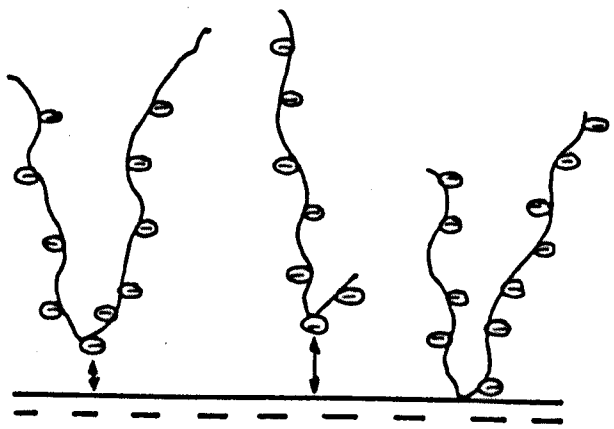
would be favoured by a high concentration of carboxylate i.e. adsorption would increase with increasing pH. Finally if mechanism (2) was correct then no adsorption would take place in a system devoid of such ions.

Experimental results indicated hydrogen bonding to be the most probable method of anionic polyelectrolyte adsorption on kaolinite. However, other studies (35) have shown that the presence of polyvalent cations increase the sedimentation rates of kaolin suspensions.

As previously described this indicates increased adsorption of polymer by anchor points, or electrostatic bridges. However, an excess of anchor points may in fact flatten the polyacrylamide chains and thus hinder flocculation. It therefore seems likely that, in the presence of polyvalent cations, adsorption onto kaolinite occurs via both hydrogen bonding and electrostatic bridging mechanisms. However, when the polymer charge is 100% anionic, repulsive forces do not allow sufficiently close approach for adsorption to occur, consequently considerable decreases in settling velocities are obtained. This situation is depicted in Figure 4.12.

The apparent lack of shale flocculation with cationic polymers is also unusual since at first sight it might be envisaged that a cationic polyelectrolyte would be most suitable for flocculating a negatively charged mineral suspension (32). In fact it appears that the polymer chains probably become strongly attracted, by electrostatic forces, to the surfaces of the shale. A certain degree

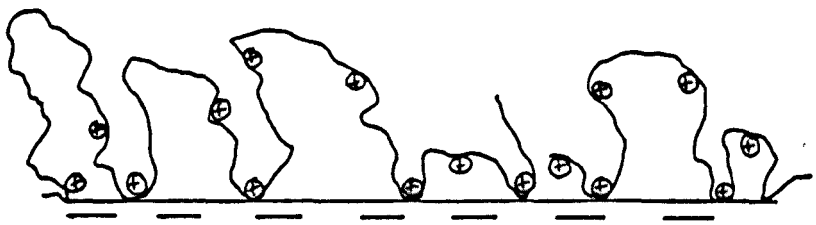
Figure 4.12 Adsorption of 100% Anionic Polymer onto Shale Surface



Adsorption reduced due to electrostatic repulsion overcoming bonding forces.

of flattening of the polymer is therefore likely making it less available for bridging. This is shown diagrammatically in Figure 4.13. As a general rule an increase in cationic character is likely to be followed by a decrease in the settling rate of shale, because of the loss of extended chains in solution.

Figure 4.13 Adsorption of Cationic Polymers onto Shale Surface



Electrostatic attraction leads to loss of extended chains for bridging.

Anionic polymers were also found to be effective flocculants for coal. This was again due to hydrogen bonding between the unionised carboxyl and/or amide groups of the polymer and surface active groups on the coal, as well as electrostatic bridge formation, due to interaction with calcium ions in solution and surface oxygen atoms. When employing cationic polymers in contrast with the low shale settling velocities obtained, improved success was achieved with the coal slurries. Electrostatic attraction would still influence polymer adsorption but due to the reduced negative charge on coal (108) this effect would be decreased and thus less detrimental to the bridging process than in the case of the shale.

In the virtual absence of electrostatic interactions it seems likely that the principle mode of attachment of non-ionic polyacrylamides (which may contain a small proportion of anionic groups) is hydrogen bonding. The fact that non-ionic polyacrylamides will

flocculate clay-type materials without first reducing the zeta potential (22) shows that the electrical double layer is not so strong as to prevent particles coming within bridging range of one another as is the case with some anionic polyacrylamides.

4.1.4 Summary

Interpreting the conclusions from the settling tests as a whole it was anticipated that, due to differences in the ratios of coal/shale settling velocities with the various polymer types, selective flocculation behaviour may be expected in a mixed system. The following section describes subsequent work on the separation of coal/shale slurries.

4.2 SELECTIVE FLOCCULATION TESTS

The results of the settling tests on separate coal and shale slurries indicated that, for cationic polymers, the relative settling ratios of coal and shale were of the order 3:1, whereas for anionic polymers, a maximum ratio of 1:18 was produced. Similar settling velocities for both coal and shale had been obtained using a non-ionic polymer. Thus it was possible to propose that, in a mixed system, cationic polymers would produce selective flocculation of coal while anionic polymers would produce selective shale flocculation. Non-ionic polymers would be unlikely to result in any selectivity.

In order to verify these proposals, separation tests were conducted on a 50/50 w/w mixture of coal and shale. The overall ash content of this material was 46%.

4.2.1 Experimental

Twenty five grams each of coal and shale (i.e. 5% w/v) were added to 1 litre of distilled water containing calgon (0.5 kg/tonne[†]), Ca^{2+} (0.1 kg/tonne) and Mg^{2+} (0.09 kg/tonne). This was mixed at high speed (3,500 r.p.m.) for 1½ minutes. Reducing the speed to 350 r.p.m. the polymer was added over a period of 1 minute. It was felt that this latter speed would be high enough to provide the necessary collisions of particles for bridging to occur without creating excessive shear conditions, which would rupture flocs as they were formed. Stirring was discontinued shortly after flocculant addition was completed. A period of 5 minutes was allowed for any flocculated material to settle out, the supernatant decanted off and the remaining sediment dried, weighed and ashed (104).

Initially 0.3 kg/tonne of flocculant was added but it was clear that at this dosage, the majority of the solids were flocculated, with little or no separation apparent. The dosage was subsequently reduced until a separation was detected; in the majority of cases, this occurred at approximately 0.1 kg/tonne. The final levels decided upon were between 0.005 - 0.05 kg/tonne. A test without polymer addition was also conducted.

To establish the efficiency of the process the three dependent variables used in these tests were; ash content, weight yield and combustible recovery.

[†] 0.5 kg/tonne calgon was added in the selective flocculation testwork, as opposed to the 0.08 kg/tonne previously used in the settling tests. This was due to the fact that this higher dosage had been found to be more effective in trials being carried out in a parallel project within the Mining Engineering Department (110).

$$\% \text{ Weight yield} = \frac{C}{F} \times 100$$

$$\% \text{ Combustible recovery} = \frac{C}{F} \frac{(100 - c)}{(100 - f)} \times 100$$

where C = mass of sediment (g)

c = ash in sediment (%)

F = mass of feed (g)

f = ash in feed (%)

Ash content gives a measure of the selectivity of the process while weight yield is a function of the efficiency of flocculation. Combustible recovery is a function of both ash content and weight yield. However, as defined above, the term combustible recovery does not truly represent the combustible material in that some of the non-combustible mineral matter will be lost in the combustion process. Thus measured ash contents will be lower than the actual non-combustibles in the sample (111). However, it is considered that the expression provides a relative, if not precise, representation of combustible recovery.

Details of all of the tests are given in Appendix 3 with typical results being depicted graphically in Figures 4.14 to 4.19.

4.2.2 Discussion on Results of Selective Flocculation Testwork

Without polymer addition the ash content of the separated product was 43%, with a corresponding weight yield and combustible recovery of 46% and 48% respectively; this is compared with a feed ash of 46%. Only a slight reduction from the original 50% shale in the feed material is represented by this figure and is probably the result of its effective dispersion by calgon. Therefore, without polymer

addition it is clear that a separation produces two approximately equivalent fractions.

It is apparent from Figures 4.14 and 4.17 that, as expected, all cationic polymers exhibited selectivity towards the coal i.e. ash contents < 46% were produced. However, it was not anticipated that the addition of anionic and non-ionic polymers would also result in selectivity towards the coal. It was thought that this may have been the result of preferential adsorption of the flocculants onto the coal surface, which may have been due to several factors:

a) hydrophobic bonding at non-polar coal surface sites.

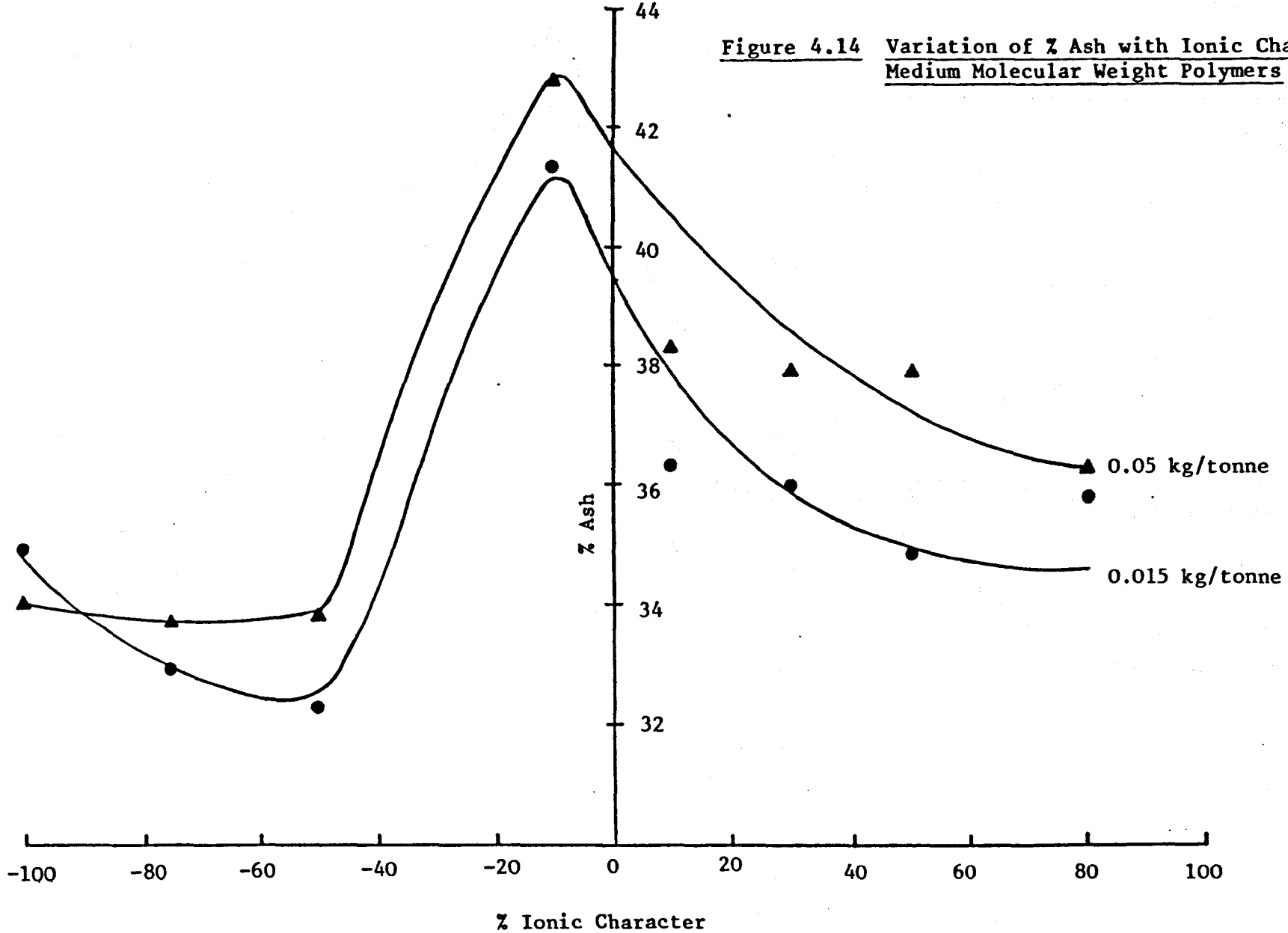
b) differences in the zeta potentials of coal and shale.

c) increased calgon dosage.

d) differences in the surface properties of the mixed mineral system from those of the individual minerals.

These being in addition to hydrogen bonding and electrostatic bridge formation previously proposed (section 4.1.3). As indicated by the relatively high ash contents of some of the sediments, particularly the anionics in Figure 4.17, it is apparent that some adsorption onto the shale surface, or shale entrapment, was occurring. On increasing the polymer dosage from 0.015 to 0.05 kg/tonne, ash contents were further increased. Settling tests had previously shown that a reduction in polymer dosage from 0.3 kg/tonne to 0.025 kg/tonne, decreased the settling velocities of shale far more than those of coal. This if selective adsorption was occurring, due to a reduction in the shale settling velocity, a lower ash product at a lower dosage would be expected; this in fact was obtained. Further support for this suggestion may be found in the tests carried out at 0.3 kg/tonne, when it appeared that in the presence of sufficient polymer all species were flocculated.

Figure 4.14 Variation of % Ash with Ionic Character
Medium Molecular Weight Polymers



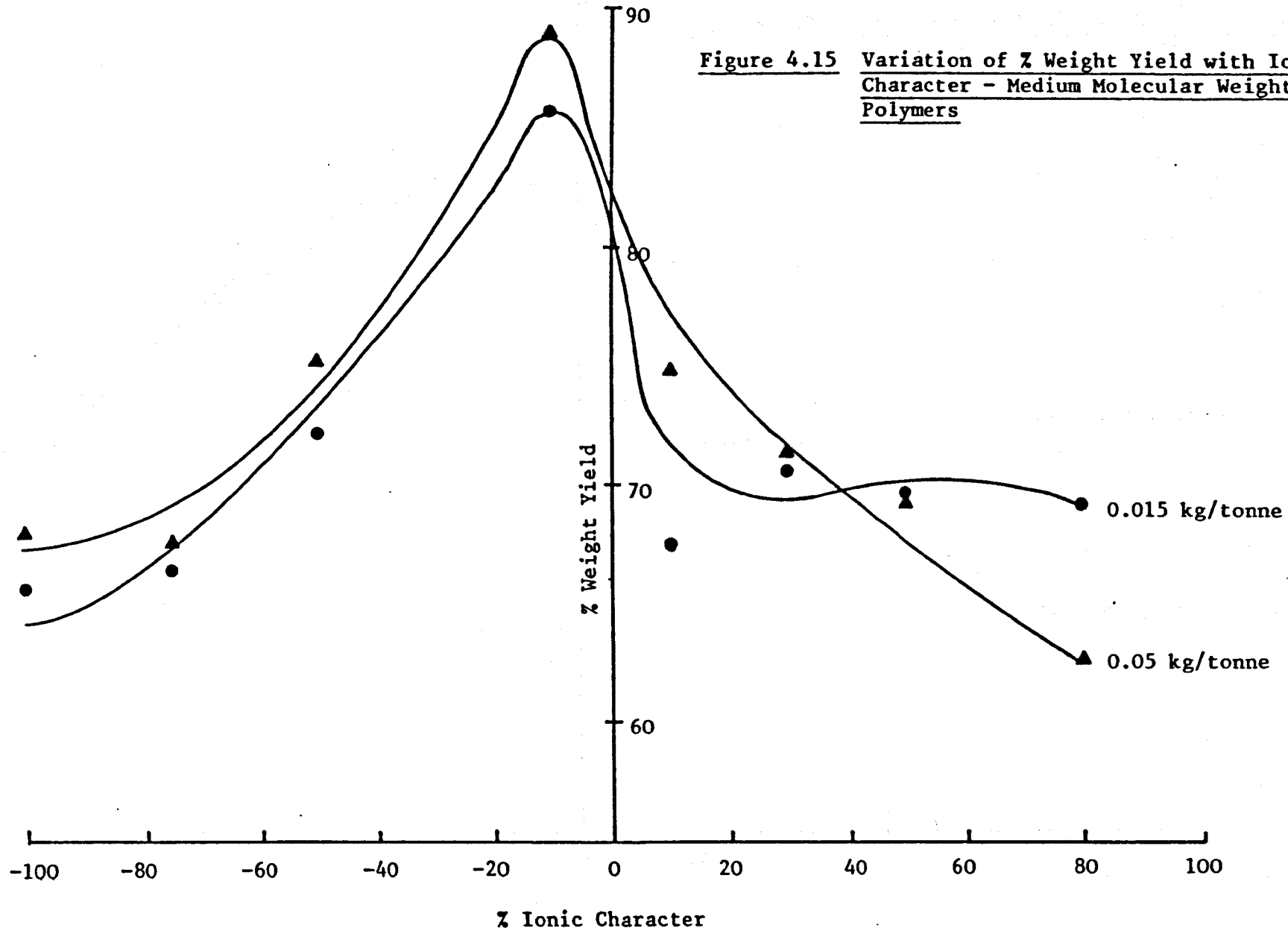
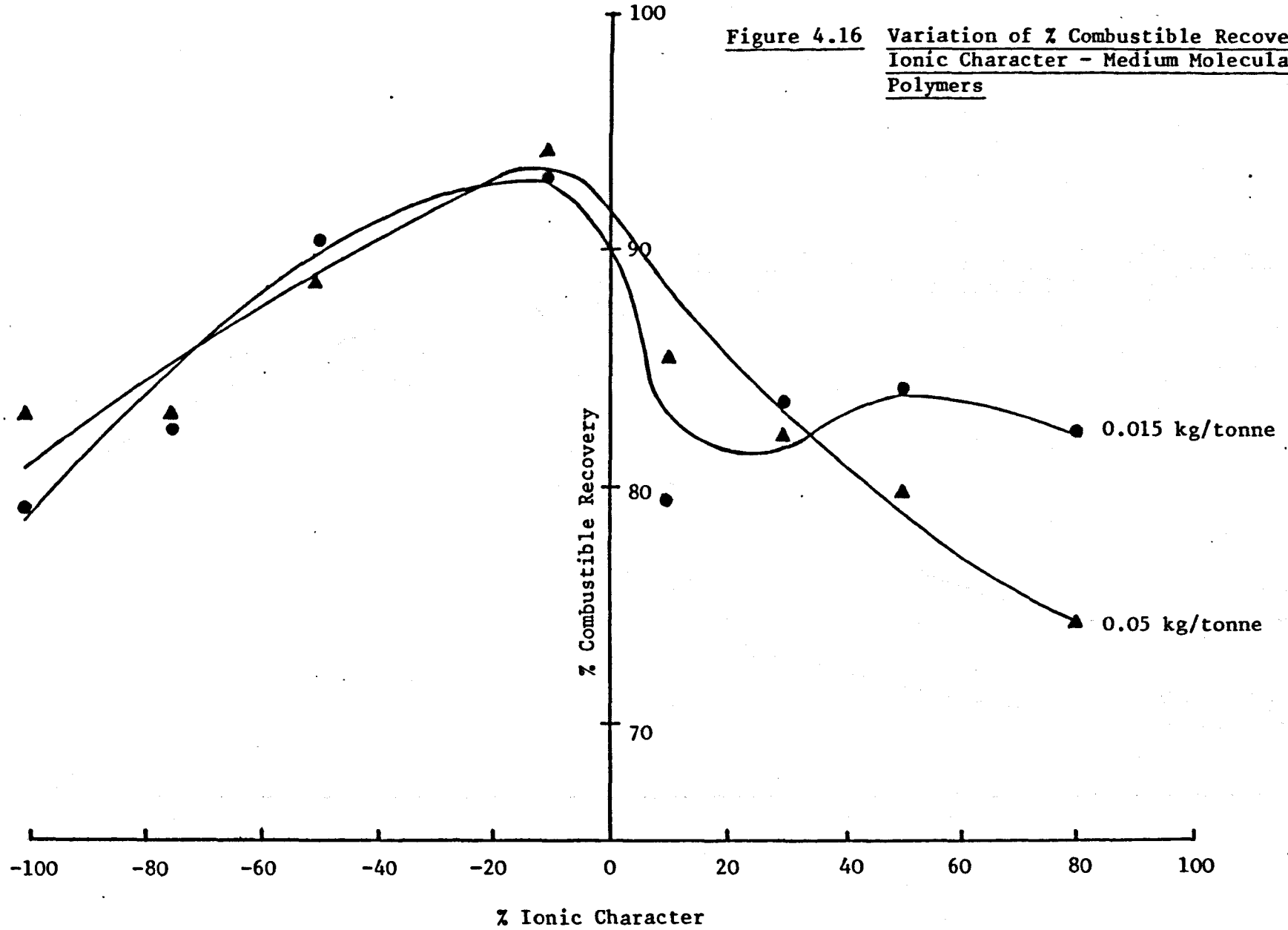


Figure 4.15 Variation of % Weight Yield with Ionic Character - Medium Molecular Weight Polymers

Figure 4.16 Variation of % Combustible Recovery with Ionic Character - Medium Molecular Weight Polymers



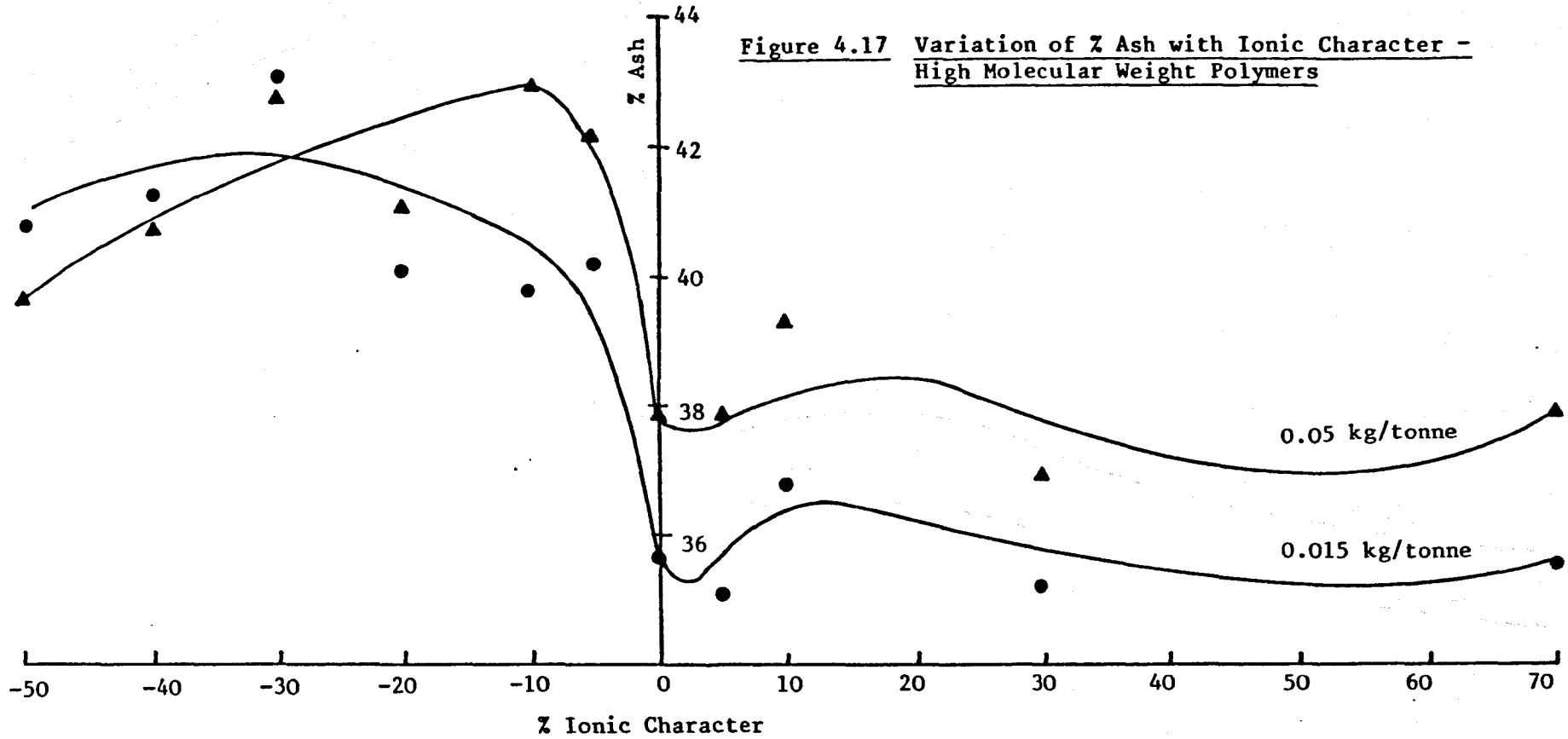
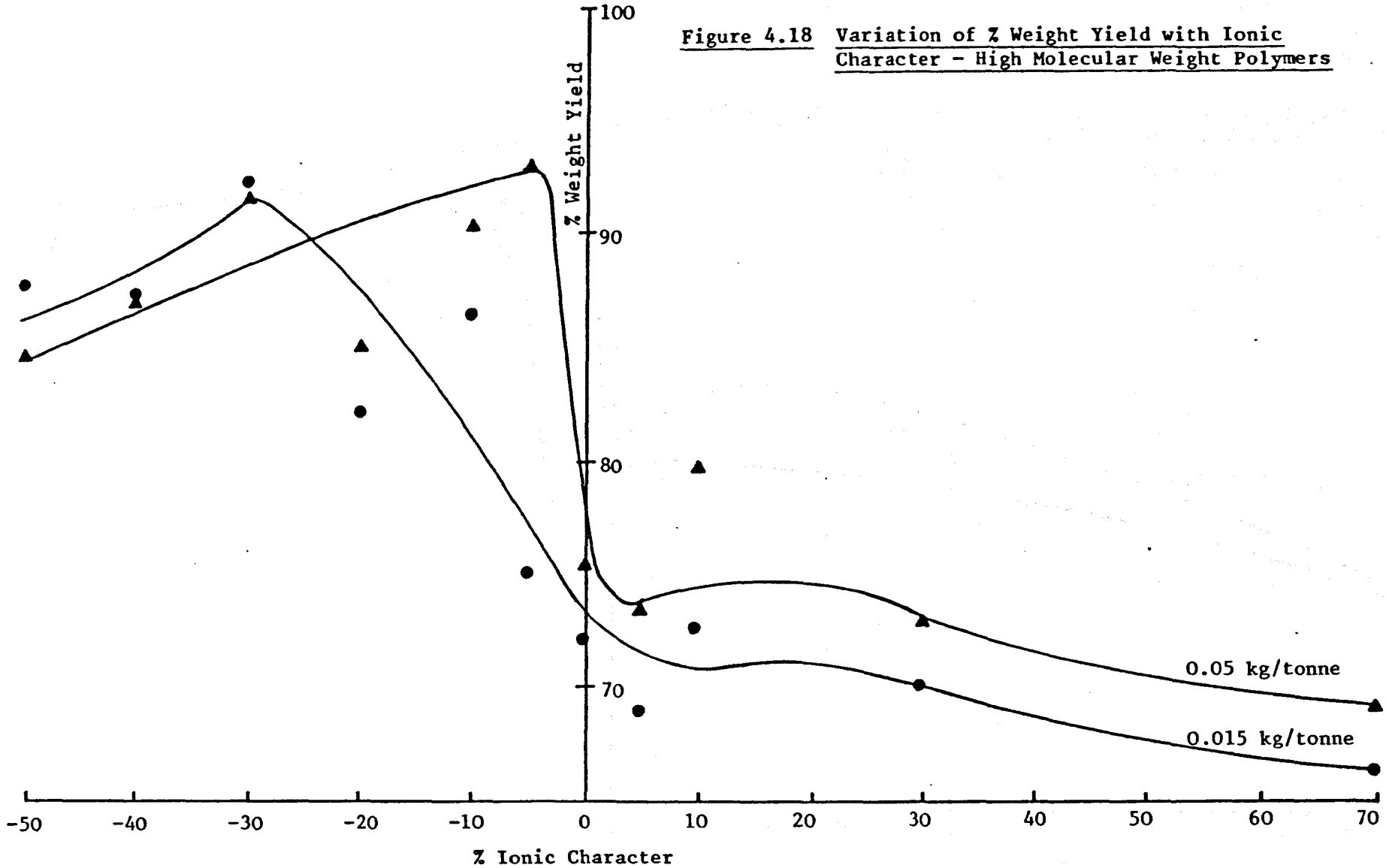


Figure 4.17 Variation of % Ash with Ionic Character - High Molecular Weight Polymers

Figure 4.18 Variation of % Weight Yield with Ionic Character - High Molecular Weight Polymers



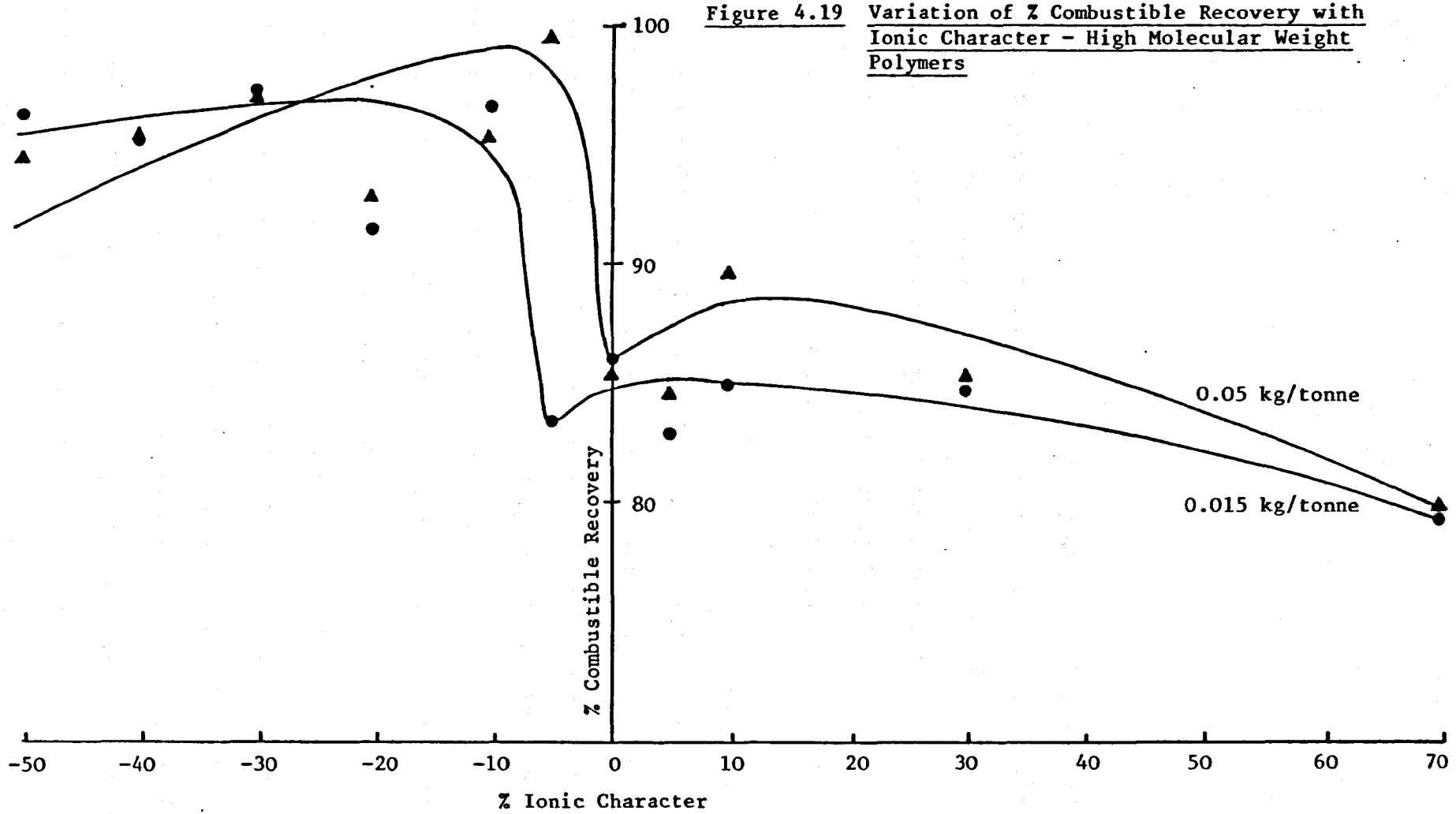


Figure 4.19 Variation of % Combustible Recovery with Ionic Character - High Molecular Weight Polymers

The curves for weight yield tended to follow those of the ash content in that when a high ash sediment was produced a correspondingly high weight yield was also obtained. This fact may have been related to the inadequacy of the separation process which suffered from two major problems. The first was that flocculated material was unintentionally decanted off due to difficulties in establishing the interface between the flocculated and suspended material. Secondly that shale, which settled on top of the flocculated sediment (particularly evident with the high molecular weight anionic polymers) was difficult to remove by decantation. The recoveries achieved were similar to those obtained in industrial flotation, but with such correspondingly high ash contents there is an obvious need for a further cleaning stage(s). Due to the various molecular weights and ionic characters of the flocculants used, no detailed explanation of the actual form of the individual curves can be given. Both the distribution of molecular weight and position of ionic charges could have also contributed to the nature of the results obtained.

As a result of the difficulties encountered, using the decantation technique, it was felt that improvements would probably be achieved using a separating funnel. This is shown in Plate 2 and was subsequently utilised in all further testwork. Table 4.1 indicates the magnitude of reductions in ash content which were achieved using this technique.

PLATE 2

YREX

Table 4.1 Comparison of Separation Techniques

Polymer	Decantation Sediment % ash	Separating Funnel Sediment % ash
A6	40.0	34.6
NI	35.3	34.7
C1	34.8	32.4
A7	32.4	31.5

4.2.3 Summary

It is apparent that, using all types of polyacrylamide polymer, selective flocculation of coal/shale mixtures could be achieved. In all cases coal was the major flocculated component. It is also clear that the use of a separating funnel, produced superior ash contents to those obtained by decantation. However, due to the wide variations in molecular weights and ionic characters it was very difficult to isolate the effects of polymer characteristics on selective flocculation. Tests using polymers of constant ionic character and varying molecular weights were thus required. Polymers of this type were manufactured by Allied Colloids. While these were being prepared it was decided to investigate the electrokinetic properties of coal and shale, before examining the effects of pH on selective flocculation. These tests together with those relating to the effects of solids concentration and an initial investigation into promoter addition are described in the following sections.

4.3 EFFECT OF pH ON THE ZETA POTENTIALS OF COAL AND SHALE

It was considered that a knowledge of the zeta potentials of both coal and shale, at various pH values, would be advantageous for two main reasons. The first was that they may help to clarify some of the assumptions concerning the mechanisms involved in polymer adsorption onto coal and shale surfaces, made in previous sections (4.1.3 and 4.2.2). Secondly since the effect of pH was to be studied at a later stage these may also give some indication of the changes in surface potential, and thus highlight any changes in the various modes of adsorption which might be expected to occur.

4.3.1 Theoretical Aspects of Microelectrophoresis

The technique of microelectrophoresis was chosen for the determination of zeta potentials of coal and shale due mainly to its previous wide use in the mineral processing field (112, 113) and its availability within the Mining Engineering Department at Nottingham University. As a result, details of this technique only are given; others have been described briefly in section 2.2.1.

Microelectrophoresis is the measurement of the velocity of charged particles suspended in a liquid under an applied electric field. The electrophoretic mobility, defined as the velocity per unit field strength, is the quantity obtained directly from experimental observations, thus:

$$\mu_\varepsilon = \frac{V_e}{E_z}$$

where μ_ε = electrophoretic mobility

V_e = particle velocity

E_z = field strength = $\frac{\text{applied voltage}}{\text{interelectrode distance}}$

This may be converted to zeta potential (ζ) using the Smoluchowski equation (114a)

$$\mu_\varepsilon = \frac{\varepsilon_r \varepsilon_o \zeta}{\eta}$$

where ε_r = relative permittivity of suspending liquid

ε_o = permittivity of a vacuum

η = viscosity

It is usually assumed that $\varepsilon_r \varepsilon_o = \varepsilon$ the permittivity of suspending liquid,

hence,

$$\mu_\varepsilon = \frac{\varepsilon \zeta}{\eta}$$

Using S.I. units with μ_ε expressed in $m^2 sec^{-1} volt^{-1}$ and taking

$\varepsilon = 6.937 \times 10^{-10}$ Faradays per metre
$\eta = 8.903 \times 10^{-4}$ $Nm^{-2}s$
} for distilled water at 25°C

The above equation then reduces to:

$$\zeta(\text{volts}) = 12.83 \times 10^{-5} \mu_\varepsilon$$

This equation is applicable to particles of all shapes and orientations, but is based on the following assumptions:

i) the double layer thickness is small in comparison with the particle radius.

ii) the viscosity and permittivity have the same values within the double layer and bulk solution.

iii) the particle is non-conducting.

iv) the applied electric field can be simply added to the field of the electric double layer.

v) the velocity gradient begins at the particle surface.

Various other derivations have been made which necessitate calculation of particle radius and double layer thickness. However, it was felt that, in this study, the Smoluchowski equation would produce adequate results, since an exact number for the zeta potential was not required, rather a comparison between figures obtained for coal and shale at the various pH values.

4.3.2 Choice of Cell

The equipment used for the testwork was the Rank Brothers Particle Microelectrophoresis Apparatus Mark II, shown in Plate 3. It can be used with either circular or rectangular cross sectional silica cells; both of these have their advantages (115).

Those of the circular cell are:

i) a smaller electric current and less errors due to polarisation occur, since this cell is of smaller cross sectional area than the flat cell.

ii) the volume of the cell can be made very small.

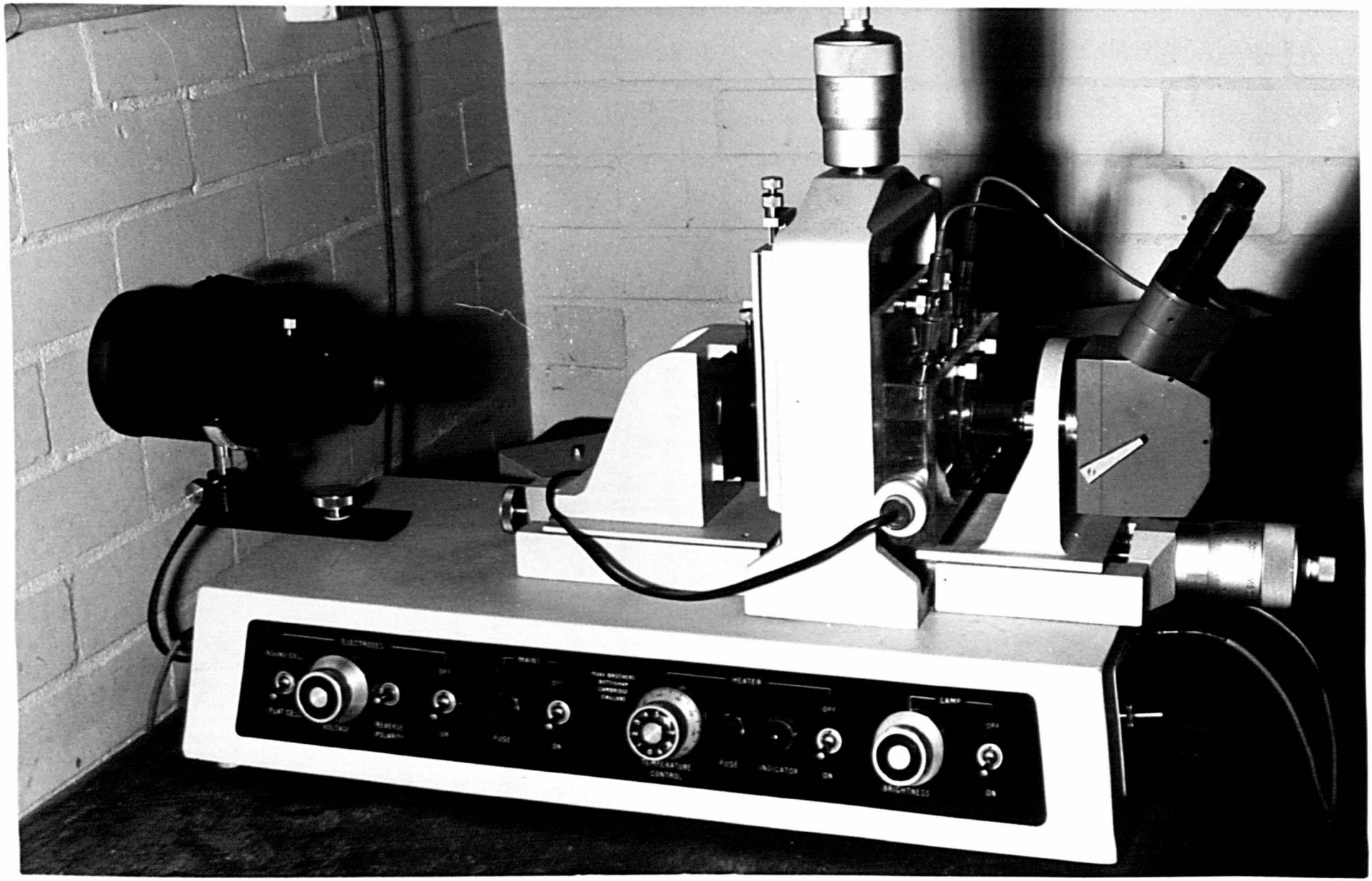
iii) side illumination of the cell may be used for observation of very small particles.

iv) by effective thermostatting, convection currents can be virtually eliminated.

The advantages of the flat cell are:

i) optical corrections are unnecessary due to the fact that fractional depths in the cell are not affected by the solution in the cell.

PLATE 3


ELECTRODES
OFF
REVERSE POLARITY
ON
MAINS
OFF
FUSE
ON
HEATER
OFF
TEMPERATURE CONTROL
FUSE
INDICATOR
ON
LAMP
OFF
BRIGHTNESS
ON

ii) at any particular level within the cell, the whole of the field of view is at this level and consequently all particle velocities are independent of their position in the field of view.

iii) particles falling under gravity forces do not alter the position of the stationary level (see later).

iv) the cell is easily constructed and much stronger.

The flat cell was chosen for practical reasons, namely that it is more robust and more easily cleaned. Since, due to direct illumination, convection currents may occur within the cell, the light source was switched on only during observation of the particles and the cell was placed in a thermostatically controlled bath at 25°C. The flat cell is illustrated in Plate 4.

4.3.3 Determination of Interelectrode Distance

In order to determine field strength, and ultimately zeta potentials, the distance between the electrodes within the cell, must be calculated. This was carried out as detailed below:

The cell was filled with a 0.10M solution of potassium chloride, the electrodes inserted and connected to a Wayne Kerr bridge. This was allowed to equilibrate at 25°C in a water bath before noting the conductance of the solution.

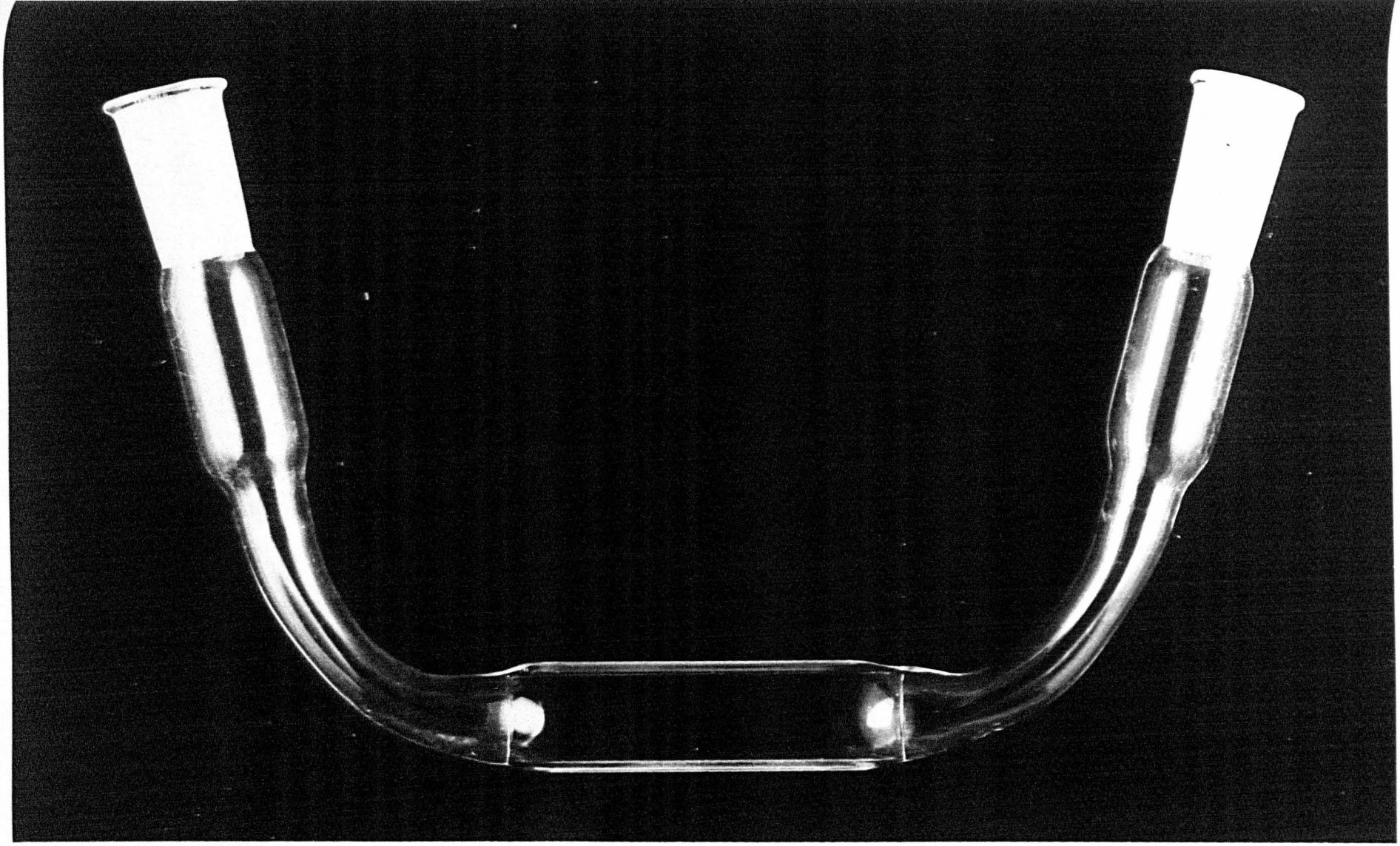
Given the equation

$$\ell = RKA$$

where ℓ = interelectrode distance (cm)

R = electrical resistance between electrodes ($\frac{1}{R} = L$, conductance) = $6.406 \times 10^3\ \Omega$

PLATE 4



K = electrical conductivity = $1.289 \times 10^{-2}\ \Omega^{-1}cm^{-1}$

A = cross section area of cell = $0.9487\ cm^2$

Then the interelectrode distance was calculated to be 7.83 cm.

4.3.4 Location of Stationary Levels

On applying an electric field across the ends of a microelectrophoretic cell both the liquid and the particles will be affected. The solution normally experiences electro-osmotic flow as a result of the charged cell walls. The observed particle velocity, V_o, is the sum of the absolute particle electrophoretic velocity relative to a stationary liquid, V_p, and the liquid velocity relative to the stationary surface, V_L. Thus:

$$V_o = V_p + V_L$$

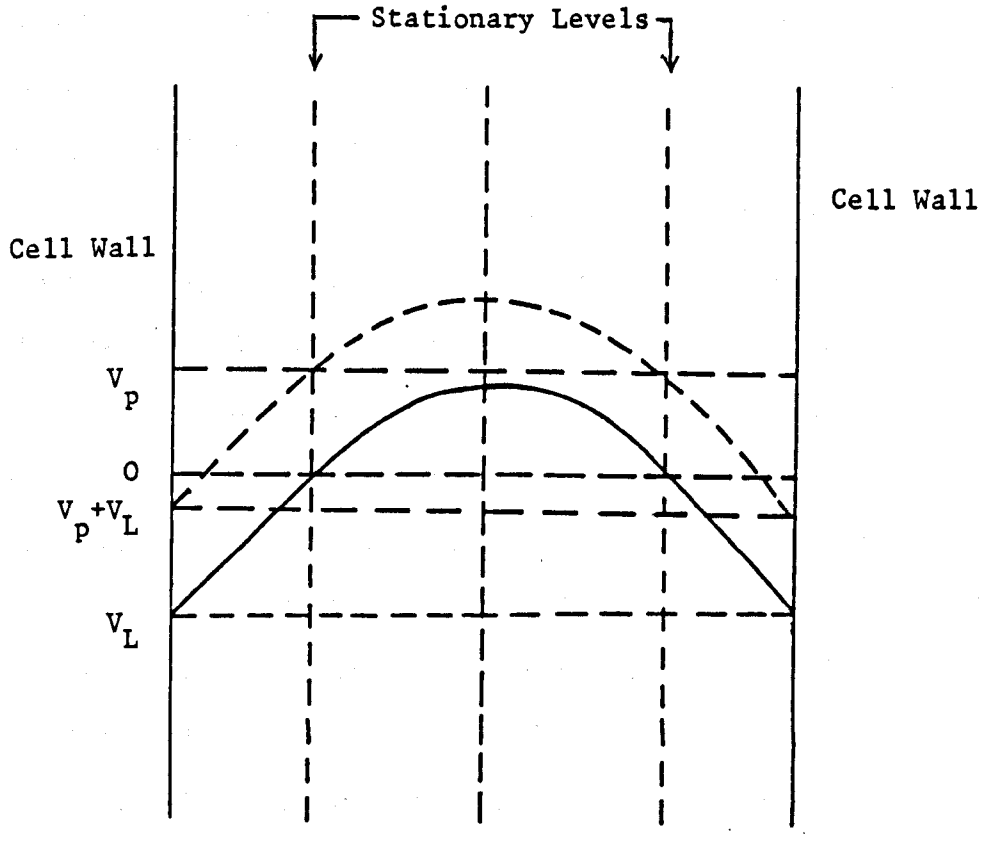
V_L varies throughout the depth of the cell while V_p remains constant at all cell depths. Measurement of the true electrophoretic velocity is therefore impossible by observation at random depths within the cell. There will however be certain levels in the cell where no net flow of liquid occurs; these positions are called "stationary levels" and it is at these levels where the measured observed velocity is the true electrophoretic velocity. This is depicted in Figure 4.20 (114b). Komagata (114c) considered the case for a flat closed cell and found that the positions were

$$x_o = 0.5 \pm (0.0833 + \frac{32}{\pi^5 k})^{\frac{1}{2}}$$

where k is the ratio of cell width to depth.

x_o is the fractional cell depth.

Figure 4.20 Velocity Profile in a Rectangular Cell



The microelectrophoretic cell used in this testwork had a k value of 9.96 and thus the stationary levels were located at 0.194 and 0.806 of the cell thickness from each wall.

4.3.5 Practical Procedure

The following procedure was used for the determination of both coal and shale mobilities.

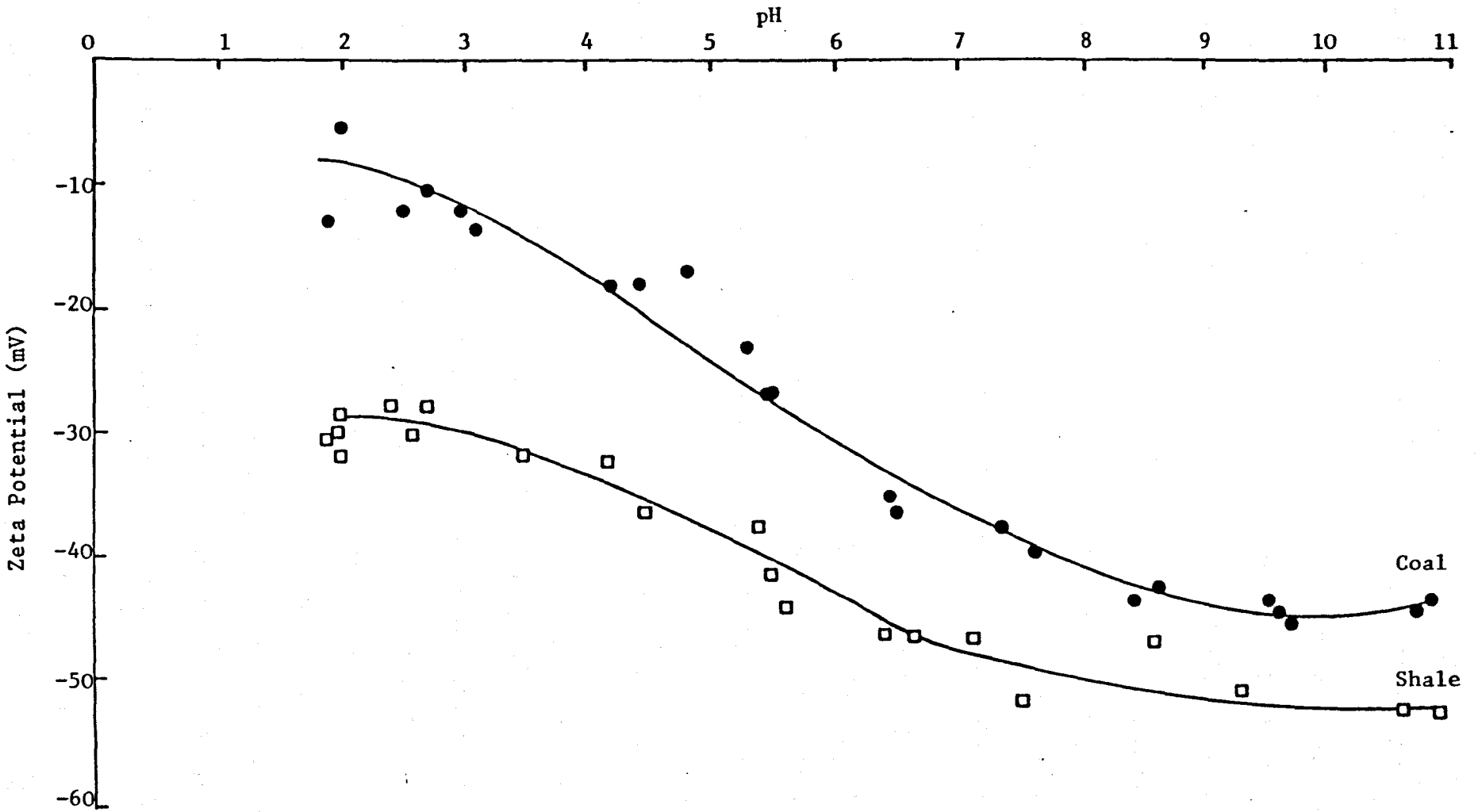
A 0.3 g sample was ground in a pestle and mortar and slurried with 300 cm^3 of distilled water containing 0.5 kg/tonne calgon, 0.09 kg/tonne Mg^{2+} and 0.10 kg/tonne Ca^{2+} (i.e. conditions similar to those used in selective flocculation tests). This was dispersed

in an ultrasonic bath for three minutes and the pH of the suspension adjusted using sodium hydroxide or hydrochloric acid. To allow "large" particles to settle out the solution was left to stand for five minutes before pipetting approximately 10 cm^3 from the top of the suspension into the cell. Once in position in the water bath, the electrodes were inserted and the cell and contents allowed to equilibrate at 25°C. One of the inside walls of the cell was focussed upon and a stationary level subsequently located. A potential difference was then applied, such that the ammeter reading did not exceed 3 mA. The time taken for a particle to traverse 100 μm was noted. In order to minimise polarisation effects the polarity of the electrodes was then reversed and a further reading taken. Ten particle velocities were recorded in a similar manner at this stationary level before moving to the other stationary level and repeating the procedure. This was in order to reduce convection current effects which may have affected the symmetry gradient of the cell.

After thorough cleaning of the cell, to minimise the effects of any impurities, this procedure was repeated at pH values from 2 to 11.

Average velocities (μm/sec), mobilities ($m^2 volt^{-1} s^{-1}$) and corresponding zeta potentials (mV) were then calculated. These are tabulated in Appendix 4 and presented graphically in Figure 4.21.

Figure 4.21 Variation of the Zeta Potential of Coal and Shale with pH



4.3.6 Discussion of the Effects of pH Variation on Zeta Potentials of Coal and Shale

The results show that at any particular pH from 2 - 11 the zeta potential of both coal and shale is negative and that, for these particular systems, the isoelectric point was not achieved. This may be a reflection of the fact that calgon, added as a dispersant, may have increased the negative zeta potentials, particularly with regard to the shale. Also the coal sample, which had been prepared in bulk and stored until required for experimentation, may have become oxidised to some extent; this would also increase the negative nature of the zeta potential.

The negative zeta potential of coal increased from about -5 mV at pH 2, to -45 mV at pH 10 - 11. This increase was probably due to the adsorption of hydroxyl ions at the coal surface, although dissociation of oxygenated surface active groups, such as carboxyl (COOH), hydroxyl (OH), and carbonyl (C=O) and methoxyl (OCH_3), may have also played a part.

The curve for the zeta potential at the surface of the shale shows a similar trend to that of coal, except that at all pH values the potential had a larger negative value; this is indicative of a larger number of charged sites at the surface.

In the selective flocculation testwork a pH of approximately 6 - 6.5 was used throughout; corresponding zeta potentials were approximately -34 mV and -45 mV for coal and shale respectively.

Two factors, both related to the zeta potential of the coal and shale, were thought to have contributed towards the fact that,

regardless of the ionic character of the polymer, coal was always the more preferentially flocculated component in a mixed coal/shale slurry.

(i) The zeta potential of the shale at the chosen pH was about 10 mV higher than that of coal. This indicates a small double layer thickness, increased charge density and a corresponding increase in repulsion between individual shale particles which polymer adsorption and bridging may be less able to overcome. Preferential adsorption at the coal surface may result. Also at this pH, water is likely to be strongly attached to the shale surface; this would minimise hydrophobic type interactions.

(ii) The dosage of dispersant (calgon) had been increased to 0.5 kg/tonne in the selective flocculation and microelectrophoresis tests. This increase may have induced an even higher negative zeta potential at the shale surface, resulting in more effective dispersion and less likelihood of polymer adsorption.

These two factors combined with the other suggestions made in section 4.2.2 are thought to be likely to account for the preferential adsorption of polymer onto coal in a coal/shale slurry.

4.3.7 Summary

A knowledge of the zeta potentials of coal and shale over a wide pH range has enabled further suggestions to be put forward regarding the apparent preferential adsorption, at near neutral pH, of all types of polyacrylamide polymer onto the coal surface. It is therefore suggested that it may also be possible to relate these zeta

potentials to the type of polymer adsorption which might be expected in the treatment of coal/shale mixtures over a wider pH range. This hypothesis is investigated in the following section.

4.4 EFFECT OF pH ON SELECTIVE FLOCCULATION

It has been shown, in section 4.3, that variations in pH affect the zeta potentials of both coal and shale suspensions; the conformation of aqueous polymer solutions are also dependent upon this variable (8a). In order to assess the importance of pH in selective flocculation, various separations were conducted at pH values between 2 and 11 using a selection of the available polymers.

4.4.1 Experimental Procedure

The procedures used for the tests were the same as that described earlier (section 4.2.1) except that before flocculant addition the separating funnel was employed and the pH adjusted to the required level, using either dilute hydrochloric acid or sodium hydroxide solution.

Combustible recoveries and weight yields were calculated as before (section 4.2.1). The sediment weights of coal and shale were also calculated using the following equation:

$$X = Yx + Z(1 - x)$$

where X = % ash in sediment (determined experimentally)

Y = % ash in shale (87.3%)

Z = % ash in coal (4.7%)

x = proportion of shale in sediment

Hence x * wt. sediment = weight of shale in sediment (g)

(weight of coal obtained by difference).

The results of all of the tests conducted are given in Appendix 5 and presented graphically in Figures 4.22 to 4.35.

4.4.2 Discussion of the Effect of pH Variation on Selective Flocculation

Throughout this testwork it was noted that the separation was difficult even when employing the separating funnel with the interface between flocculated and suspended solids being obscure. The exception was at approximately neutral pH.

(a) Anionic Polymer(s) (50%)

Figure 4.22 indicates a minimum ash content at around pH 6.3; this minimum being independent of dosage levels. Large increases in ash are noted with only small variations in pH above and below this level.

Figure 4.23 indicates maximum sedimentation at low pH values and an increasing weight yield recovery with dosage.

The sediment weights of both coal and shale, shown in Figure 4.24 are also at a maximum at low pH. However on increasing the pH to 6.3, the weight of coal in the sediment is maintained, while shale weight is reduced considerably. Both coal and shale weights, are decreased further when the pH is raised above this level, both levelling out above pH 9.

Figure 4.22 Effect of pH and Polymer Dosage on % Sediment Ash - Polymer A6

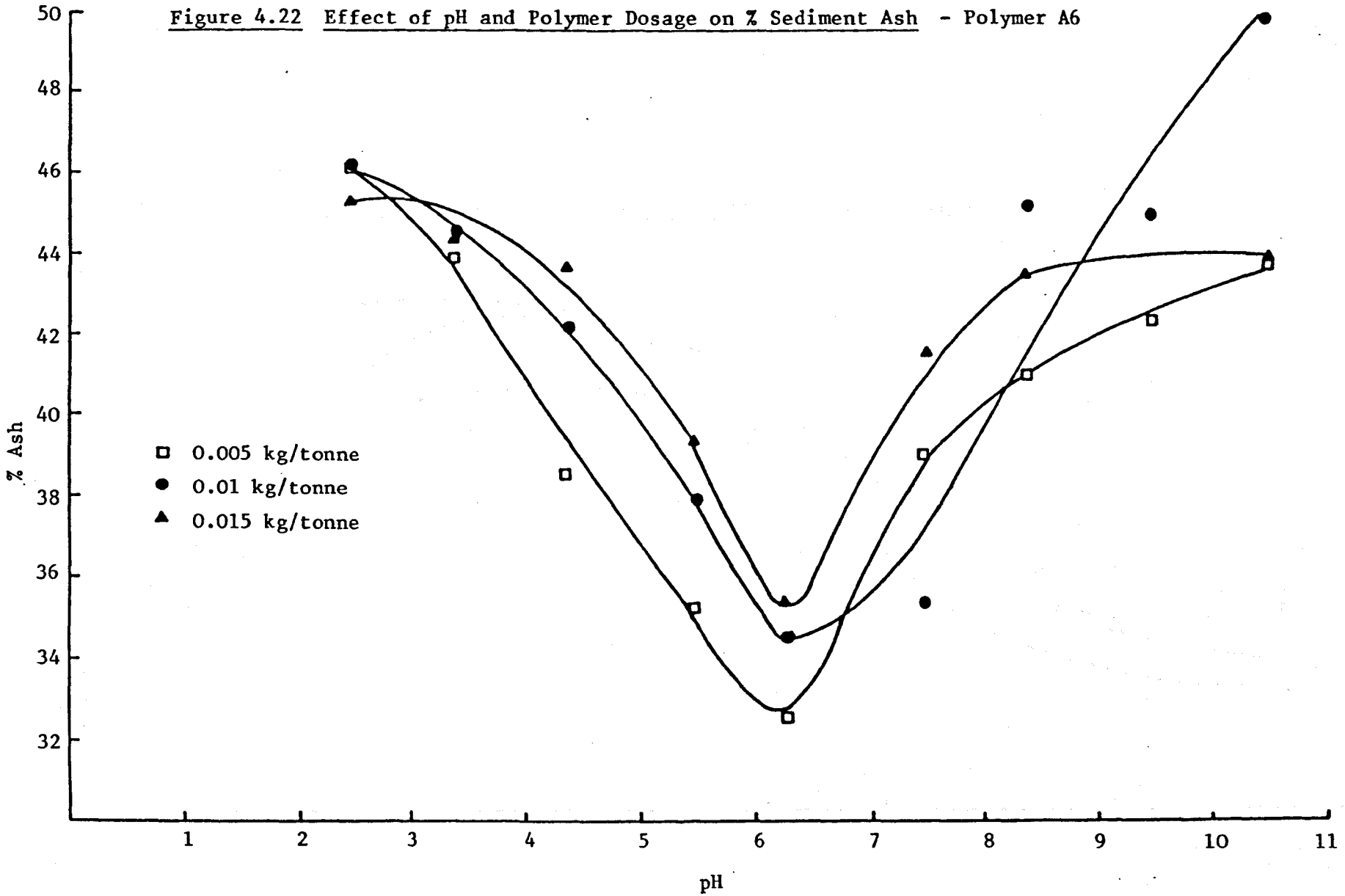


Figure 4.23 Effect of pH and Polymer Dosage on % Weight Yield - Polymer A6

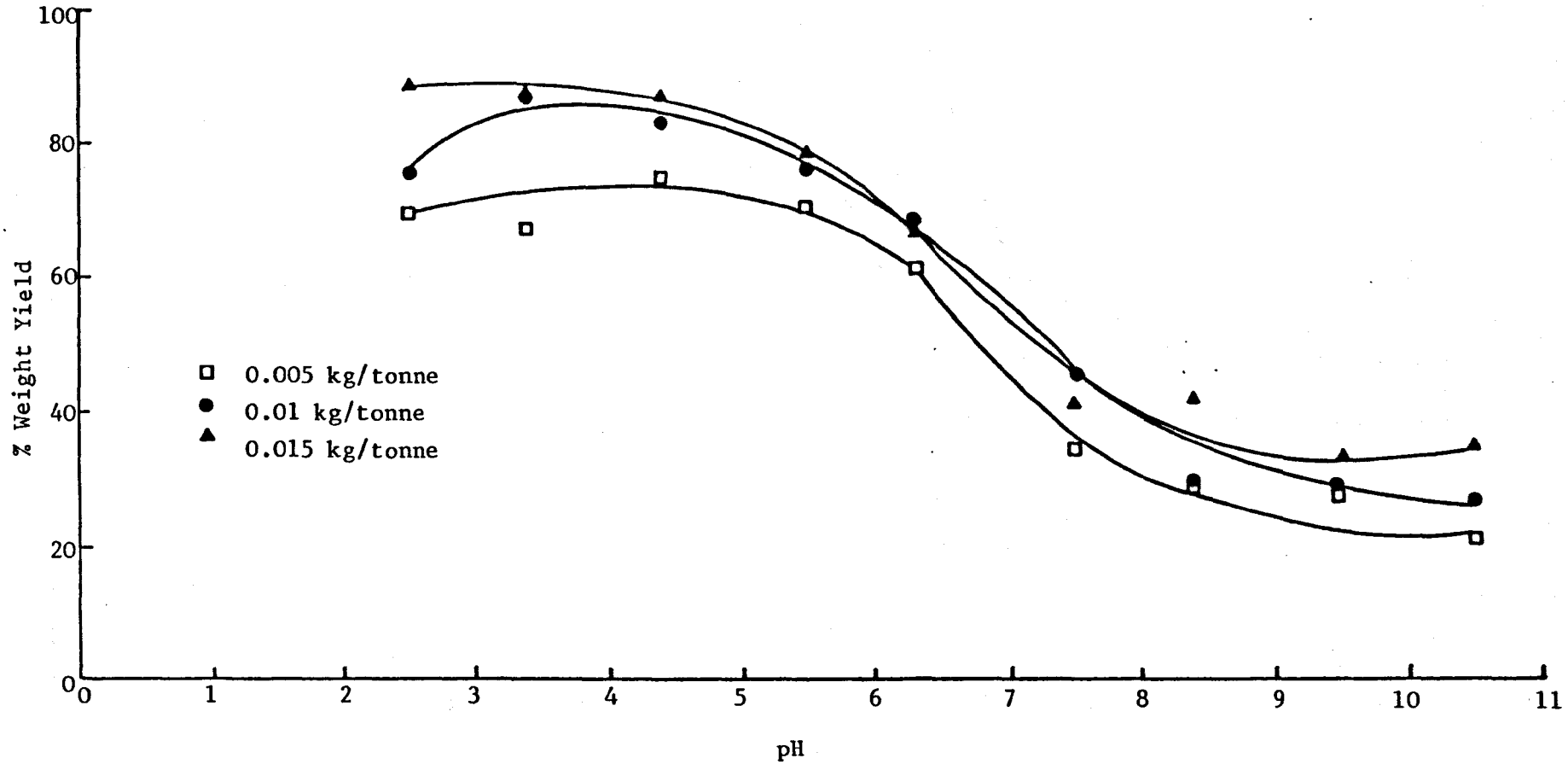


Figure 4.24 Sediment Coal and Shale Weights at Various pH Levels - Polymer A6 0.015 kg/tonne

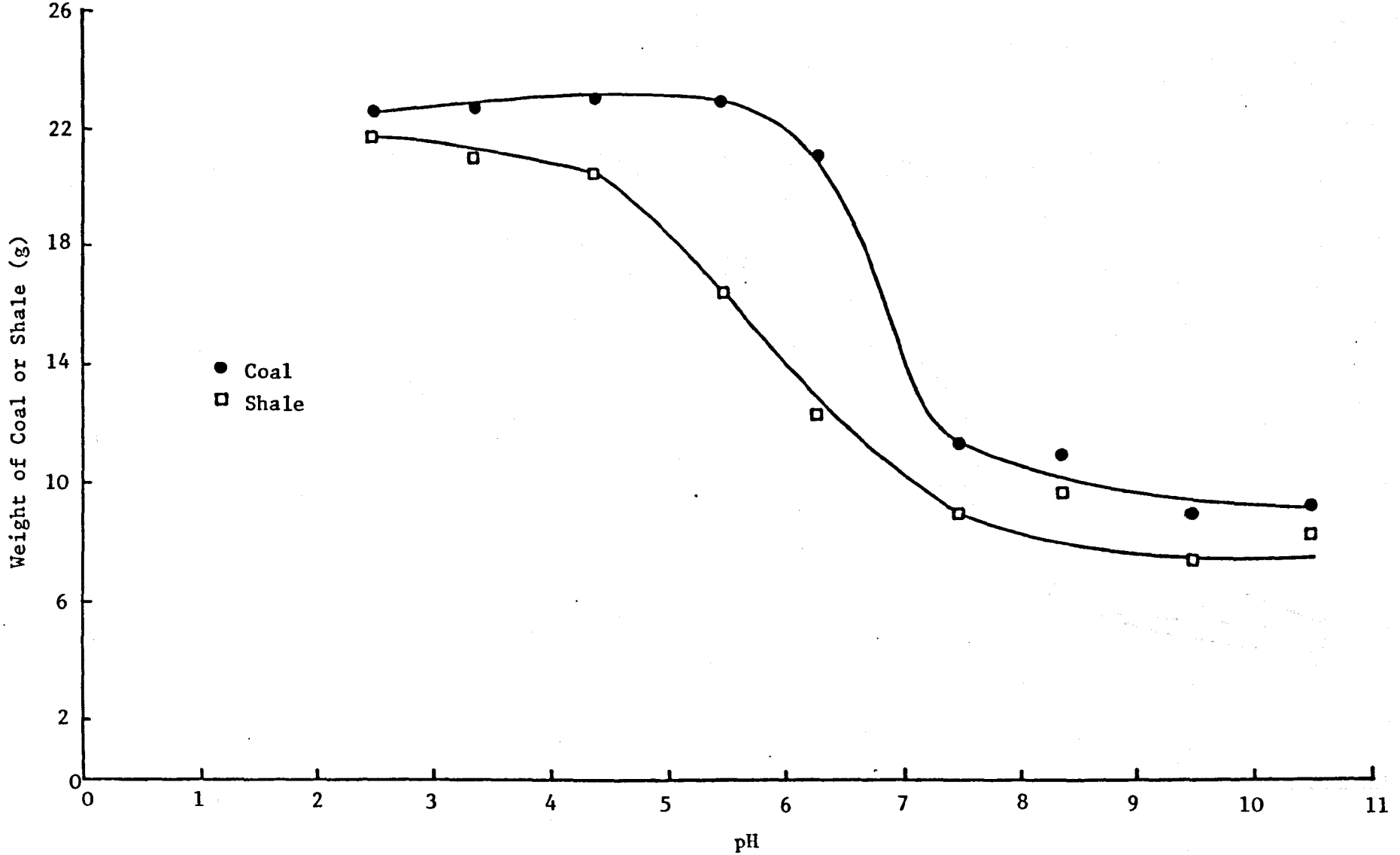
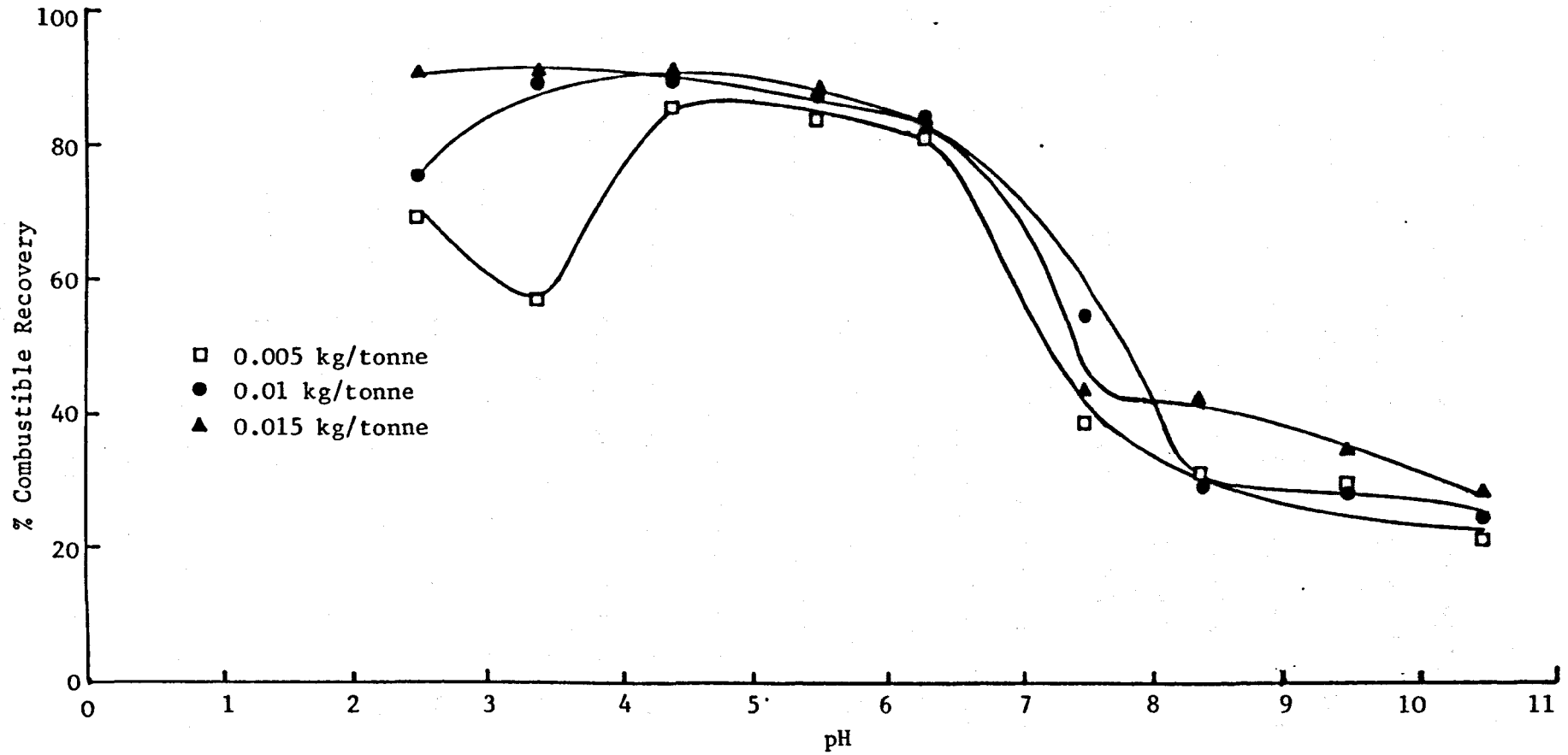


Figure 4.25 Effect of pH and Polymer Dosage on % Combustible Recovery - Polymer A6



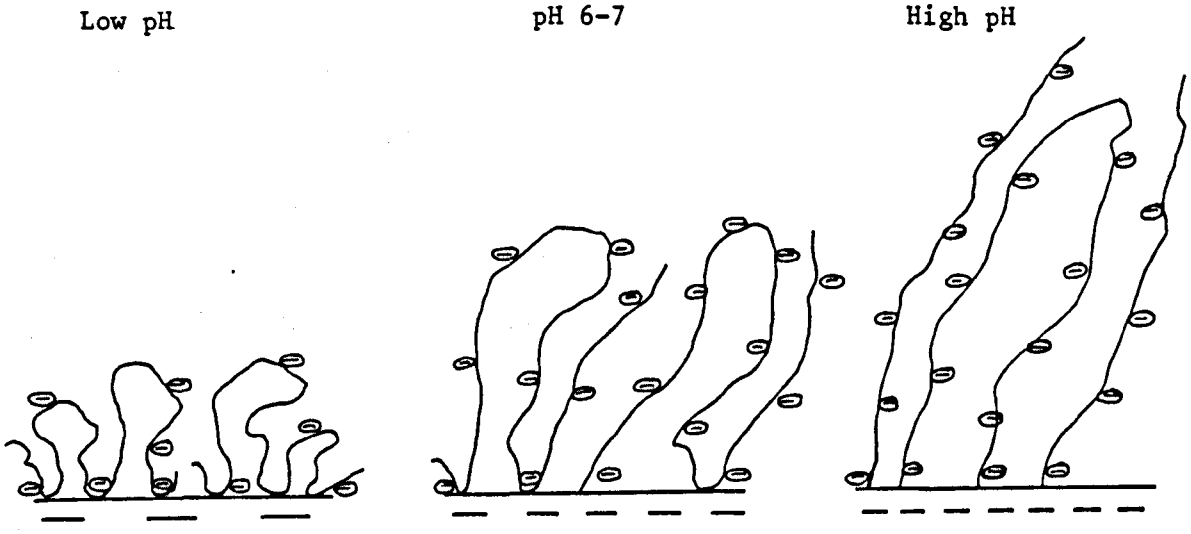
Generally, as will be shown throughout this work, the combustible recovery curve follows that of the weight yield. In Figure 4.25 variations at pH 3.5 with a polymer dosage of 0.005 kg/tonne are due to a combination of continuous increases in ash and a reduction in weight yield.

It is apparent that at low pH, since a high weight yield was achieved, flocculation was occurring. However, as indicated by the high ash content of the product, and similar coal and shale sediment weights, this was not selective. At a pH of about 6.3 the conditions were such that a low ash product having a high proportion of coal was produced. This suggests that the differences between the two systems were at their greatest at this point. At high pH, poor flocculation with little selectivity was obtained as indicated by a low weight yield, high ash product.

Considering both the changes in the zeta potentials of the minerals and the variations in polymer conformation which occur over the pH range 2 to 11, an explanation for the mechanisms involved may be attempted. The effect of pH on anionic polymer adsorption is shown diagrammatically in Figure 4.36.

At low pH levels hydrogen ions are adsorbed at the particle surfaces resulting in low zeta potentials on both coal and shale. Due to both the lack of electrostatic repulsion between the mineral surface and the polymer molecule, and negligible intramolecular polymer repulsion, the chains become coiled and adsorbed in trains, leaving few "loops and tails" for bridging. The low zeta potentials result in polymer adsorption at both coal and shale surfaces and

Figure 4.36 Effect of pH on Anionic Polymer Adsorption



lead to close particle approach, forming small tight flocs. As the pH approaches neutral, the zeta potentials become increasingly negative; improved shale dispersion, a result of electrostatic repulsion between the highly negatively charged particles, is thus favoured. Polymer adsorption, is now more feasible at the coal surface, since bonding mechanisms are able to overcome the magnitude of the negative coal zeta potential more easily than that of the shale. Moreover, increased

repulsion with the coal surface leads to polymer extension in "loops and tails", producing more favourable conditions for bridging. Ionisation of carboxylate groups occurs at pH 4 to 7, which, creates elongated polymer chains (due to intramolecular repulsions), and also favours bridging. However, increases in the pH above 7, leads to the adsorption of hydroxyl ions producing a highly negative zeta potential on both minerals. Long range repulsion then opposes adsorption, collisions between particles and polymer bridging. Any flocs which are produced will be large, weak and very easily broken by shear forces. This results in a low weight yield, high ash product and overall apparent lack of selectivity.

(b) Non-Ionic Polymers

Figure 4.26 illustrates the changes in percentage ash, combustible recovery and weight yield with variation in pH. A minimum ash content is achieved at a pH of about 8.6, but in contrast to the results with the anionic polymer, ash contents do not rise so steeply above and below this pH. Weight yield is again at a maximum at low pH with a minimum value occurring at pH 8.6. The curve showing combustible recovery again follows a similar trend to that of weight yield.

From Figure 4.27 it may be seen that maximum sediment weights of coal and shale generally occur at low pH, and that at pH 8.6, corresponding to the lowest ash product, both coal and shale sediment weights are at a minimum.

Figure 4.26 Effect of pH on % Ash, Wt. Yield and Combustible Recovery - Polymer N.I. 0.01 kg/tonne

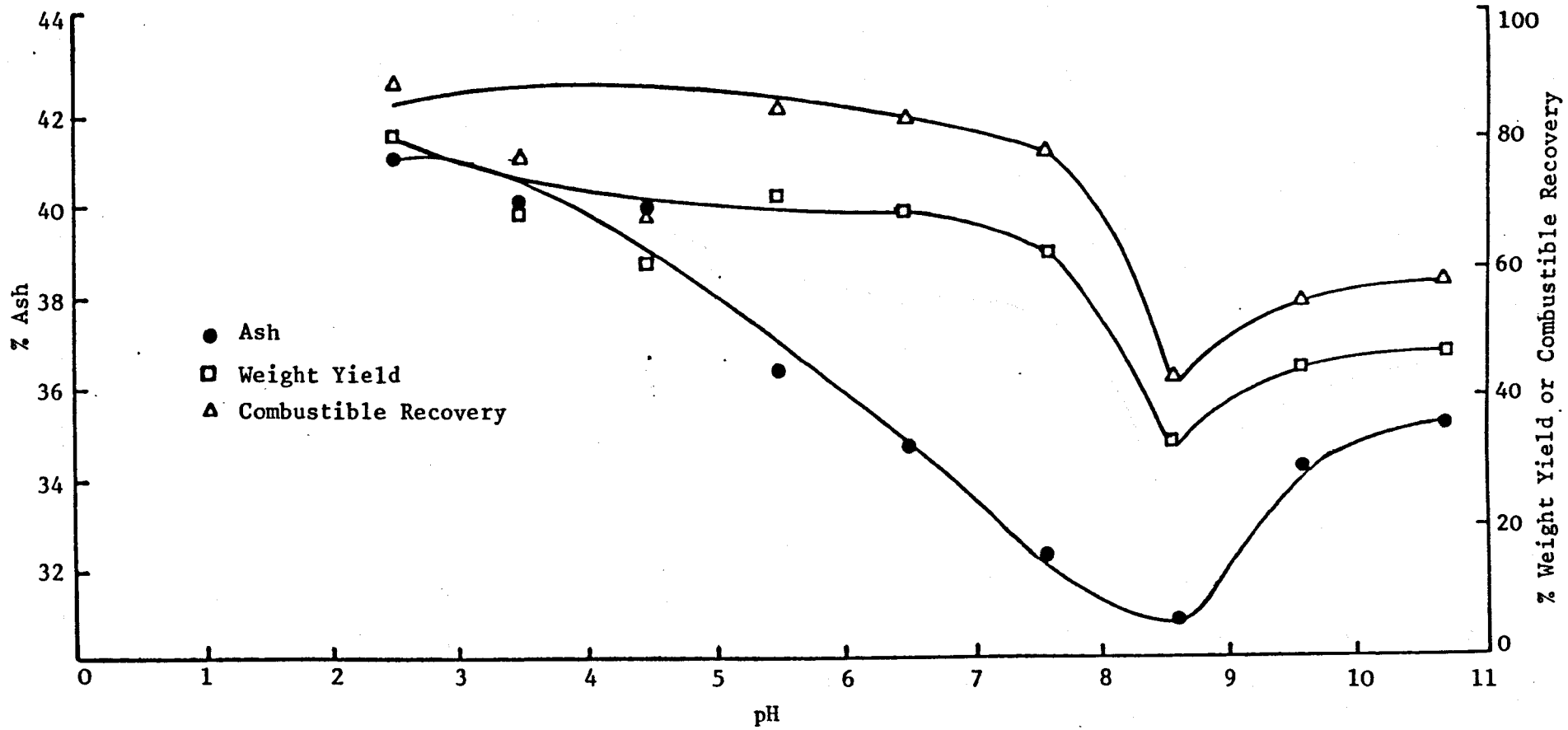
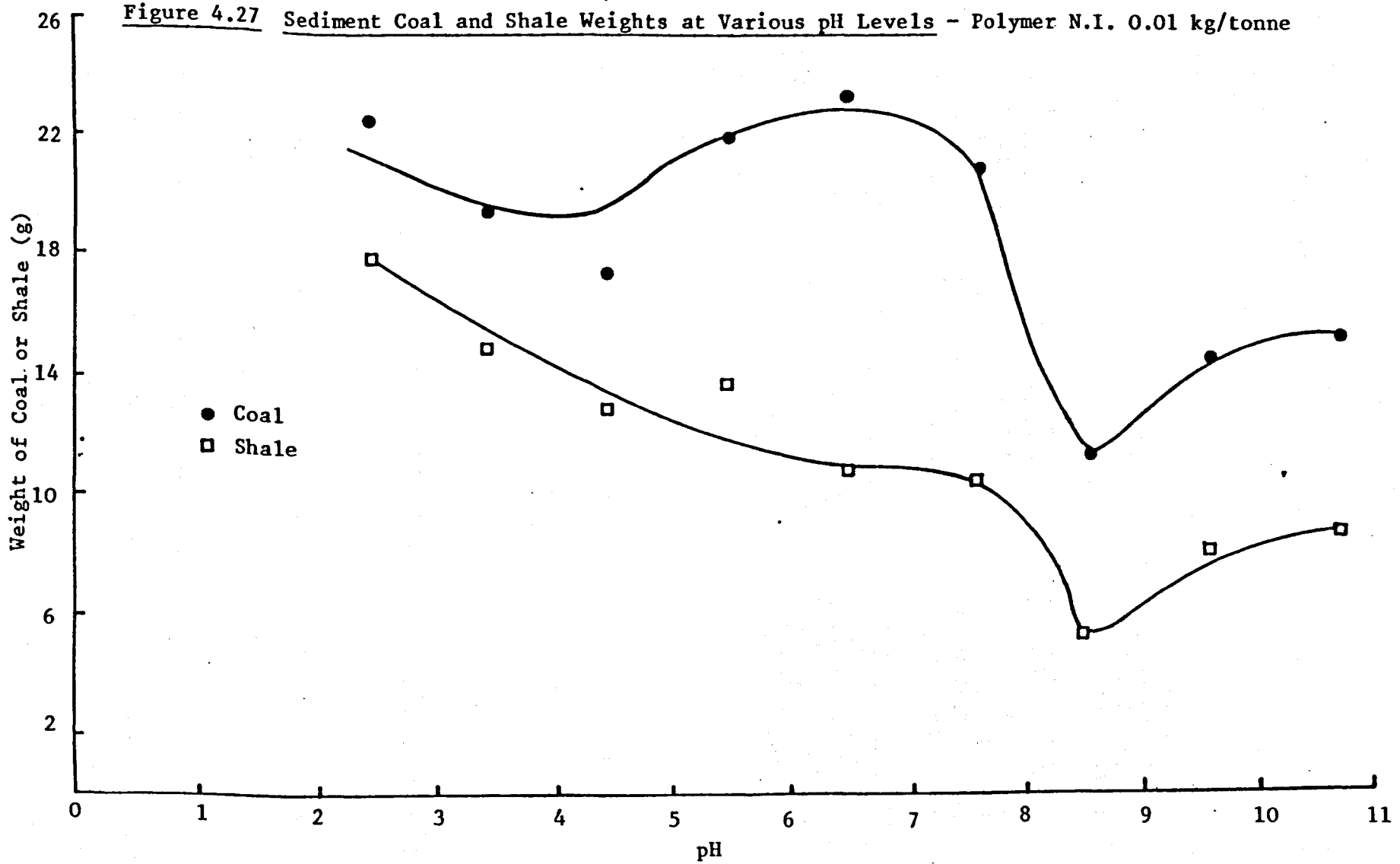


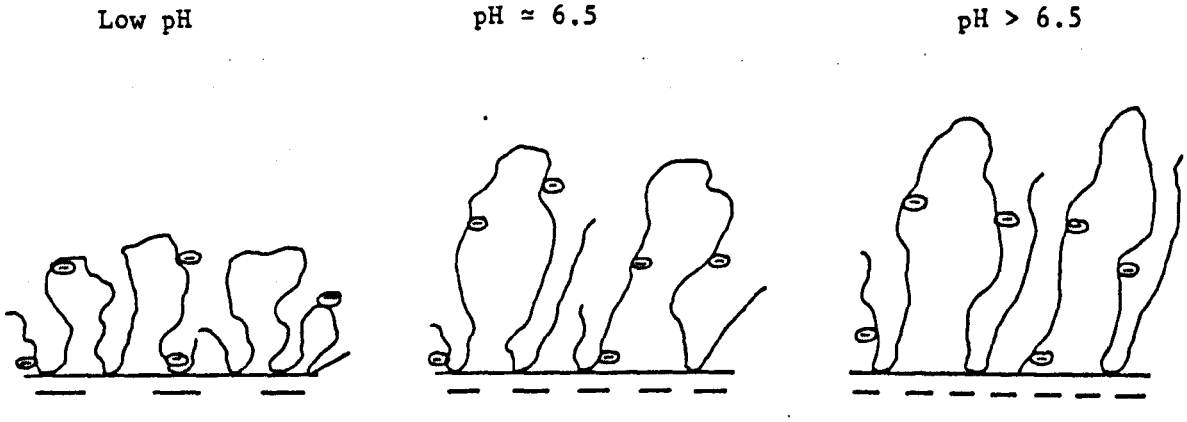
Figure 4.27 Sediment Coal and Shale Weights at Various pH Levels - Polymer N.I. 0.01 kg/tonne



Summarising these observations, it appears that at a low pH although flocculation was occurring, it was unselective. On increasing the pH, polymer adsorption at the coal surface was maintained, while selectivity towards the shale surface was decreased. At pH 8.6 and above selectivity towards the coal surface was also reduced appreciably.

Figure 4.37 illustrates the state of polymer adsorption which may be expected with a non-ionic polymer at various pH levels.

Figure 4.37 Effect of pH on Non-Ionic Polymer Adsorption



Low zeta potential, polymer coiled adsorbed onto coal and shale surfaces mainly in trains due to lack of surface repulsion and lack of extension into solution. Close particle approach and formation of small, tight flocs favoured.

Increased negative zeta potential, polymer adsorbed selectively onto coal. Existence of "loops and tails" over wider pH range, due to less intense polymer/surface repulsion, when compared with the anionics.

Hydrogen bonding, as opposed to general electrostatic interaction, will be the major bonding mechanism of a non-ionic polymer; the polymer does however inevitably contain a small percentage of anionic groups. Due to the presence of relatively few carboxylate groups, in comparison with say the 50% anionic polymer, electrostatic repulsion between the polymer and the mineral surfaces will be less intense at all pH levels. Similarly the degree of polymer extension caused by intramolecular repulsion will be reduced at pH 4 and above. As a result, at low pH, polymer chains are strongly adsorbed at many points of attachment onto all surfaces. This prevents the protrusion of long "loops and tails" and produces small tight flocs. On increasing the pH to between 3 - 6.5, due to the increased negative zeta potential, which bonding mechanisms are less able to overcome, adsorption at the shale surface is decreased. However, at the coal surface, due to less intense polymer/surface repulsion, conditions for adsorption followed by bridging are improved. As the system becomes more alkaline a decrease in adsorption at the coal surface may occur due to further increases in polymer/surface repulsion thus forming weaker, more easily ruptured flocs.

(c) Cationic Polymers (5%)

Figure 4.28 indicates a minimum ash product at a pH of between 6.5 - 8.5. Weight yield recovery is again at a maximum at low pH with combustible recovery following the same trend.

Sediment coal and shale weights (Figure 4.29) are at a maximum at low pH and, in general, decrease with an increase in pH. Optimum conditions of high coal recovery with reasonably low shale content are achieved at pH 6.7.

Figure 4.28 Effect of pH on % Ash, Wt. Yield and Combustible Recovery - Polymer C1 0.01 kg/tonne

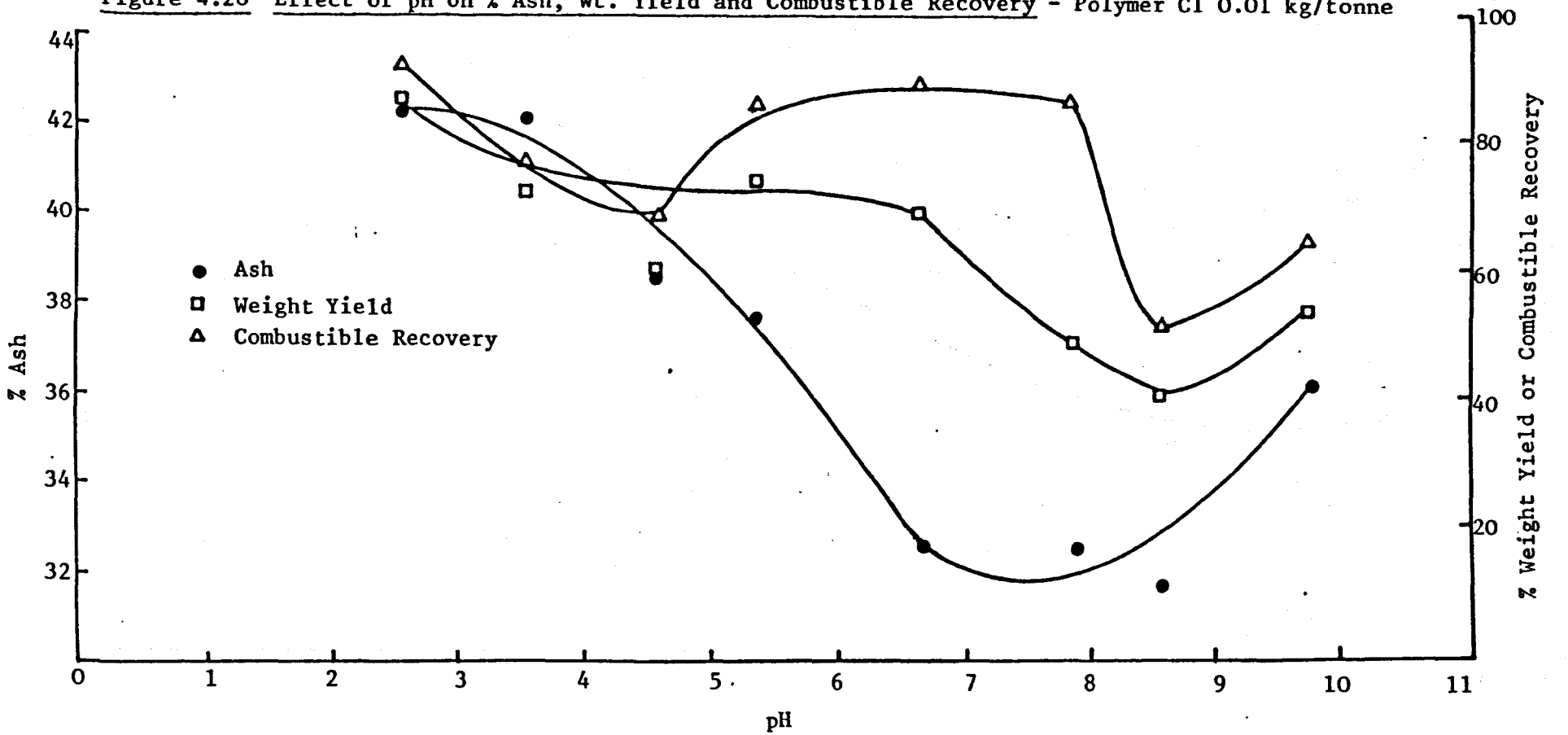
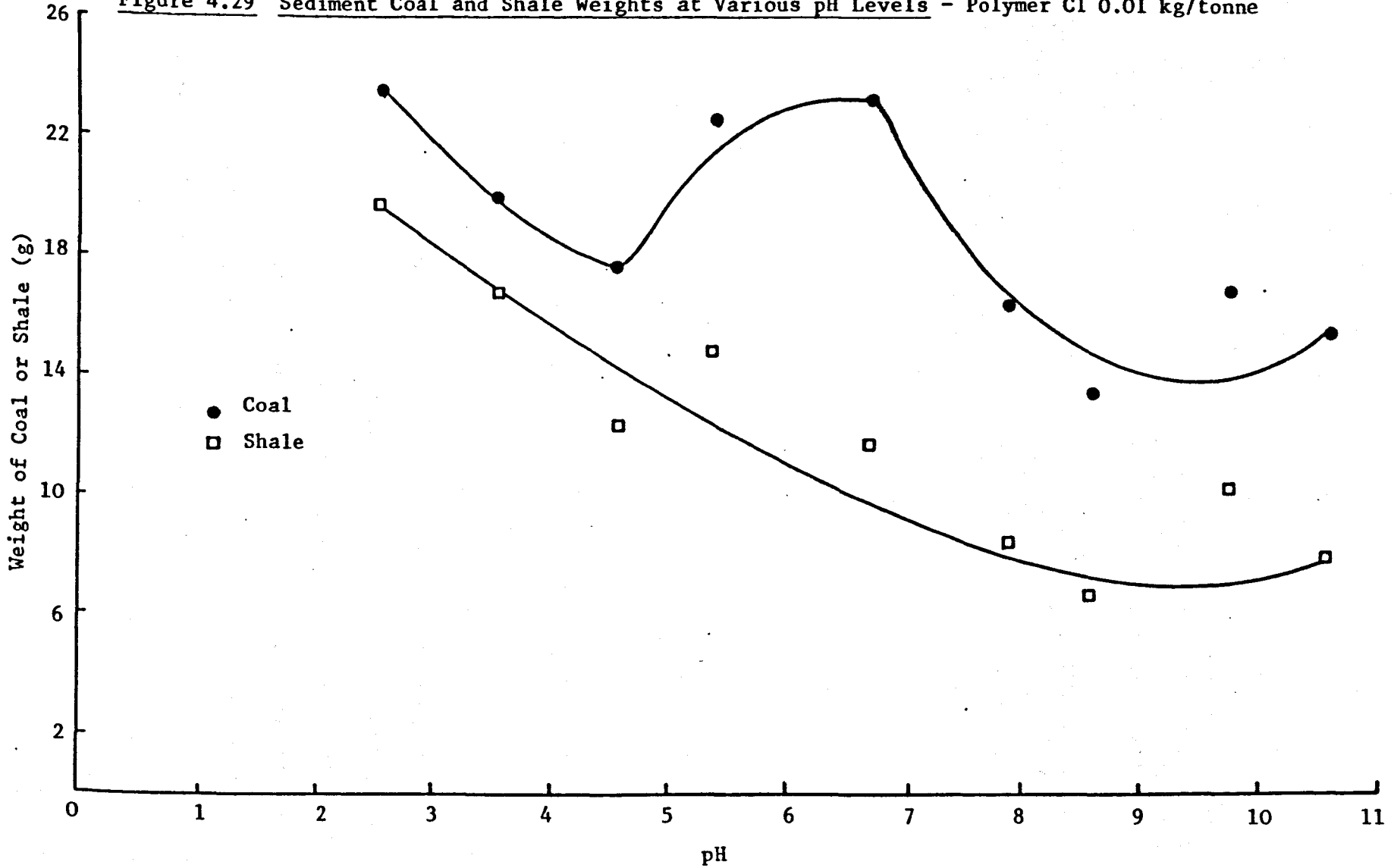
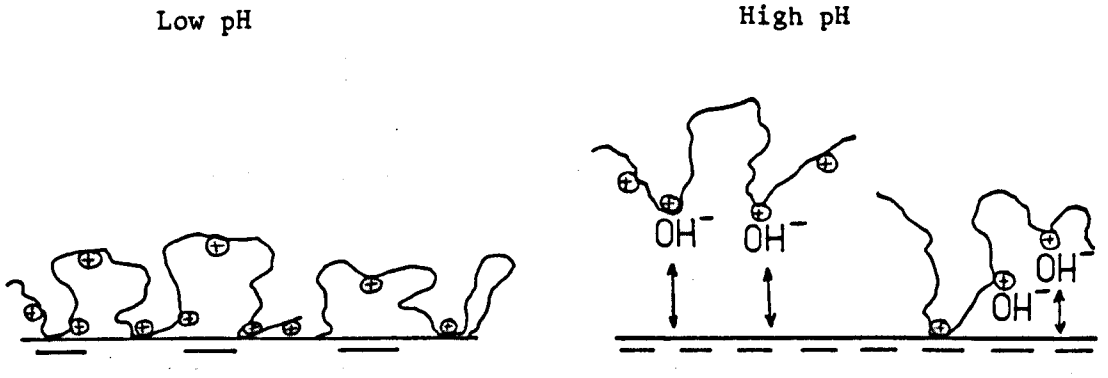


Figure 4.29 Sediment Coal and Shale Weights at Various pH Levels - Polymer C1 0.01 kg/tonne



Electrostatic attraction between polymer and mineral surfaces at low pH is such that close adsorption at the surface occurs. A flattening of the polymer chains results in some loss of bridging ability and flocs formed are small, comprising both coal and shale, with little selectivity. As the pH is increased, hydroxyl ions tend to shield the positive charge density and create electrostatic repulsion, thus hindering polymer adsorption. This is shown diagrammatically in Figure 4.38. It would appear that polymer adsorption at both surfaces is generally decreased as the pH is increased. However, due both to the lower zeta potential of coal and the presence of some hydrophobic interactions, coal recovery is

Figure 4.38 Effect of pH on Cationic Polymer Adsorption



Electrostatic attraction results in adsorption and flattening of polymer chains onto both coal and shale surfaces. Small, tight flocs formed.

Shielding of the polymer chains by hydroxyl ions produces electrostatic repulsions which hinder adsorption at both surfaces.

always superior to that of shale. At a pH of about 6.7 a balance between attractive and repulsion forces is obtained such that conditions for the optimum recovery of coal are achieved. However, polymer adsorption at the shale surface is reduced leading to lower sediment weights.

(d) Anionic Polymer (50%, medium molecular weight)

As shown in Figures 4.30 to 4.33, generally, the medium molecular weight polymer indicates similar trends to those in Figures 4.22 to 4.25. This is expected since the two polymers have the same ionic character and vary only in molecular weights. Minimum ash contents are obtained at a similar pH, but are generally lower than those in Figure 4.22. This may be due to the decrease in polymer molecular weight which will tend to reduce shale entrapment. Shale sediment weight is approximately 1.5 g (Figure 4.32) lower than that shown in Figure 4.24. The proposed mechanisms will be similar to those illustrated in Figure 4.36.

(e) Cationic Polymer (50%)

Figure 4.34 shows that, at pH 8.7, a minimum ash content of only 37.5% was obtained, indicating little selectivity. Maximum weight yields were achieved at low pH and at levels between 7.5 and 8.5. However, these did not exceed 50%. Combustible recoveries again followed a similar trend.

Figure 4.35 indicates similar sediment weights for both coal and shale at pH values up to 6.4 and at 9.6 and above. At pH 7.7 and 8.7 coal sediment weight was about 3 g higher than that of shale.

Figure 4.30 Effect of pH and Polymer Dosage on % Sediment Ash - Polymer A8

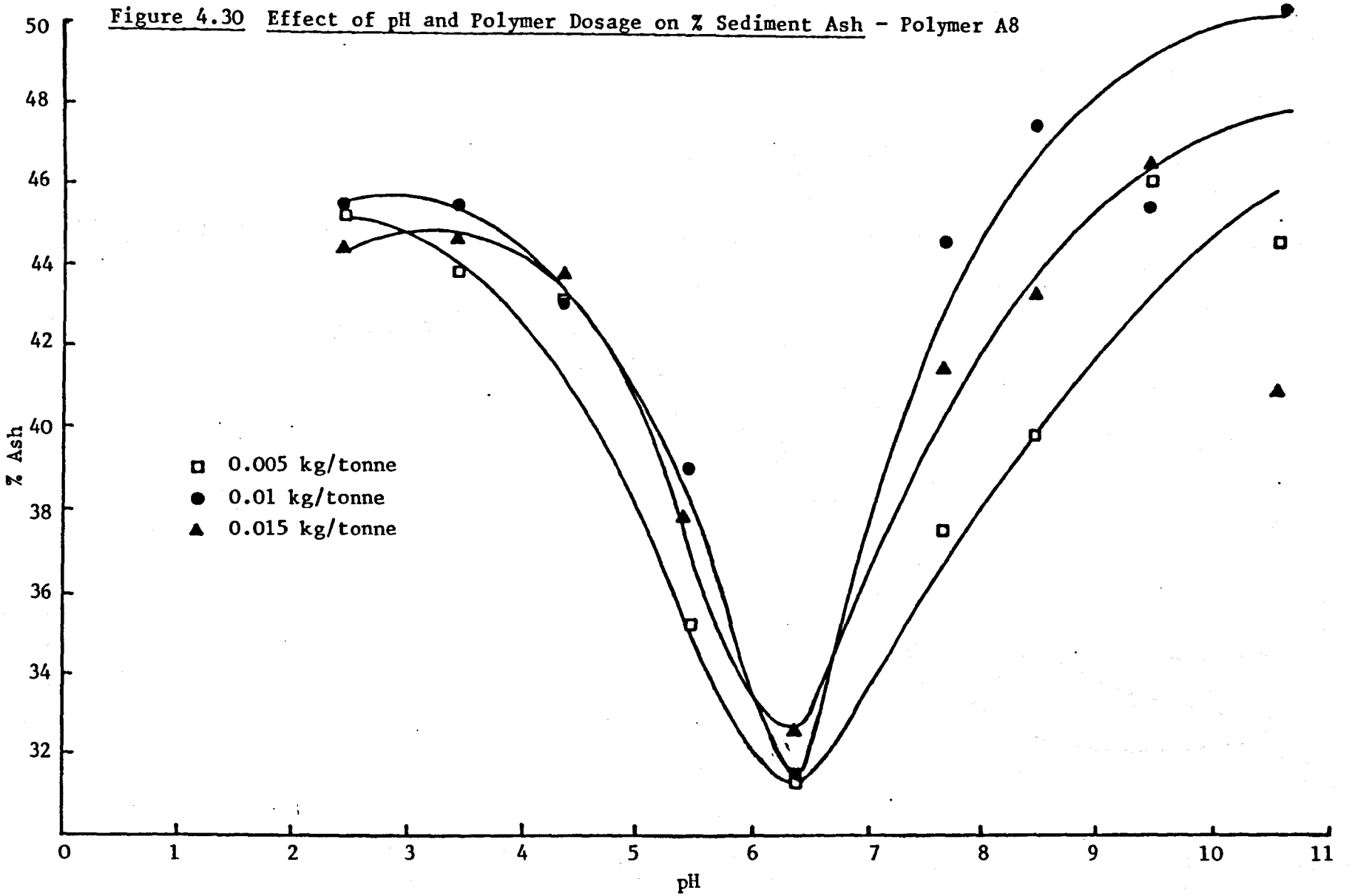


Figure 4.31 Effect of pH and Polymer Dosage on % Wt. Yield - Polymer A8

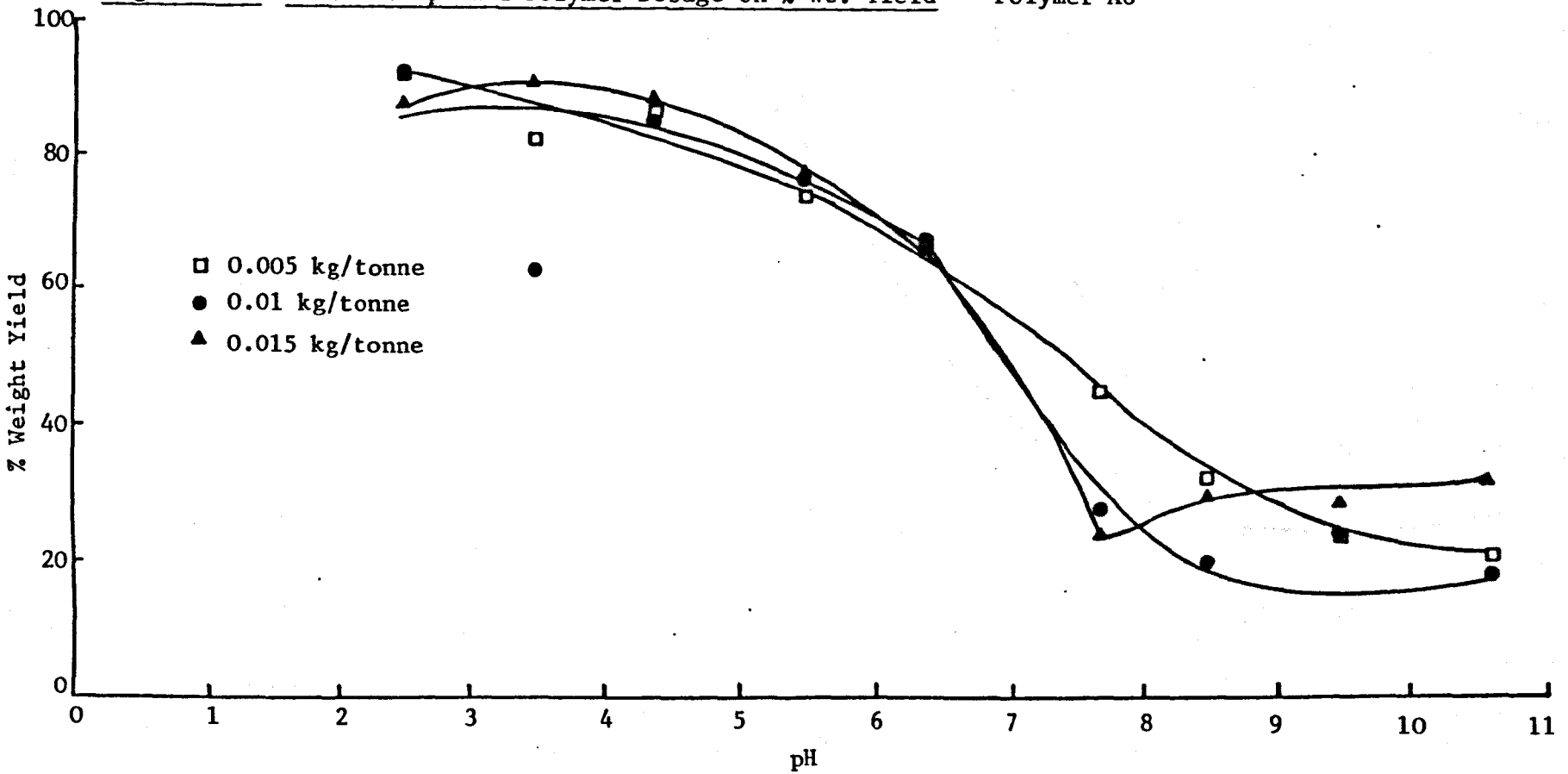


Figure 4.32 Sediment Coal and Shale Weights at Various pH Levels - Polymer A8 0.015 kg/tonne

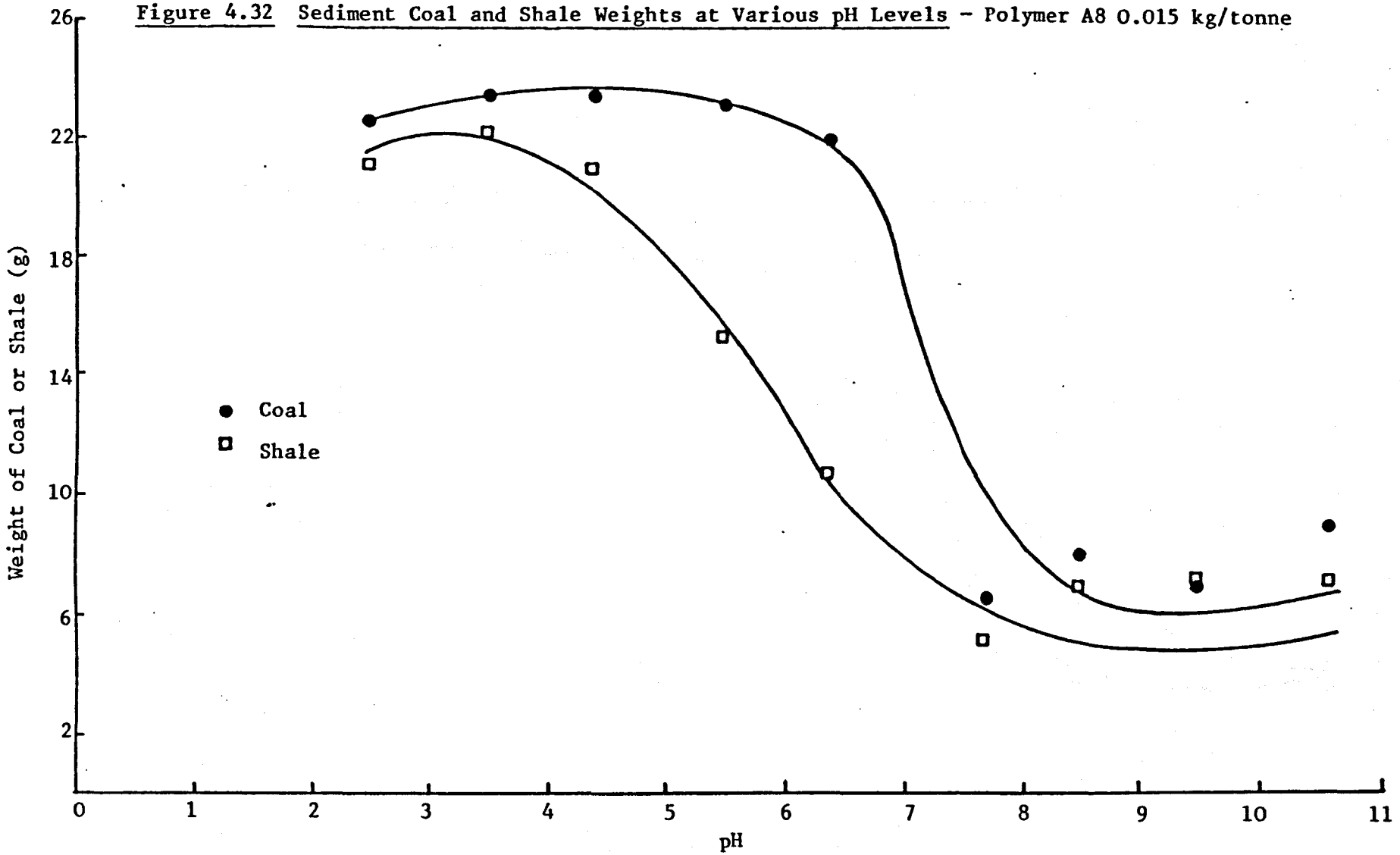


Figure 4.33 Effect of pH and Polymer Dosage on % Combustible Recovery - Polymer A8

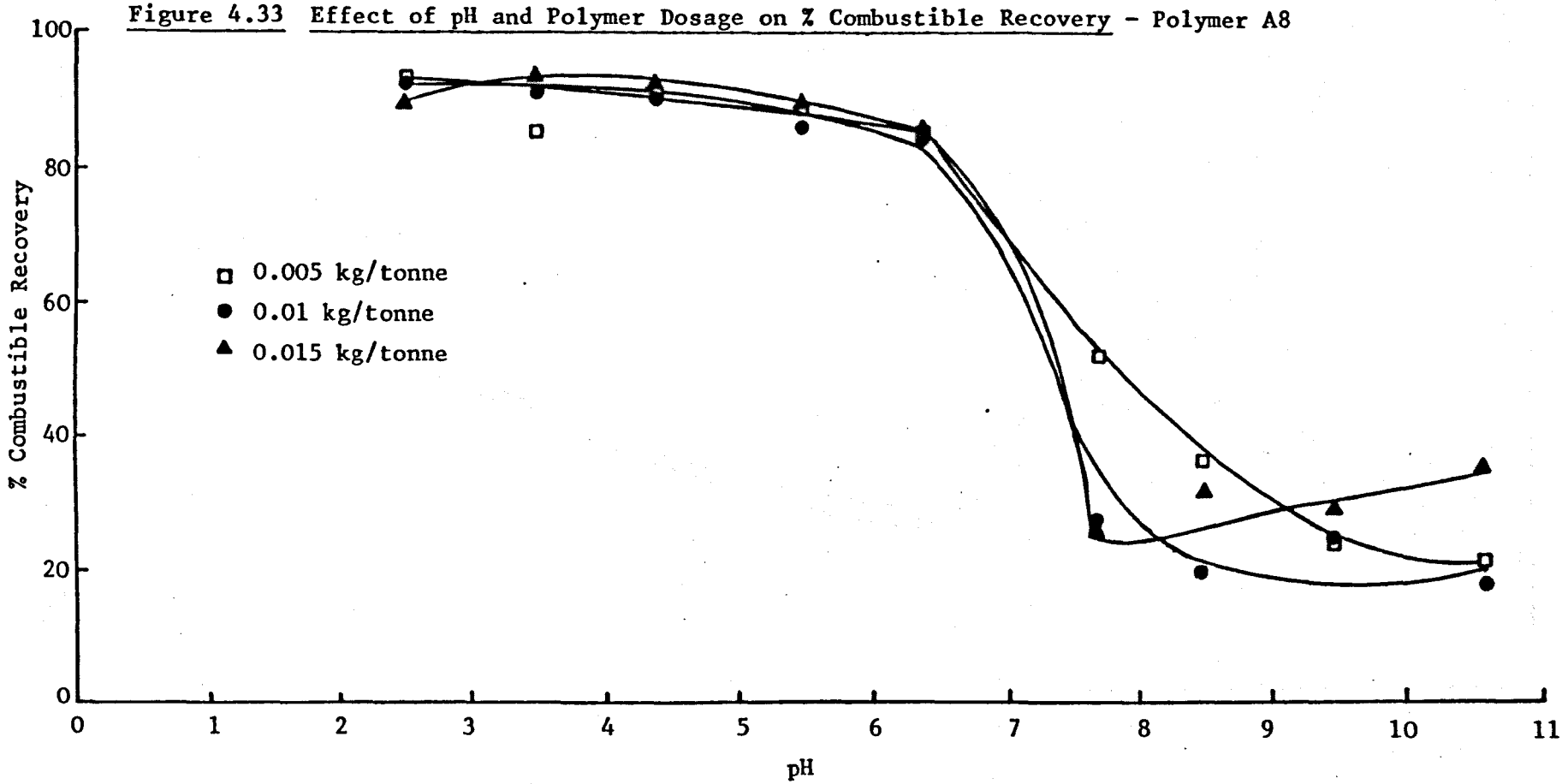


Figure 4.34 Effect of pH on % Ash, Wt. Yield and Combustible Recovery - Polymer C7 0.01 kg/tonne

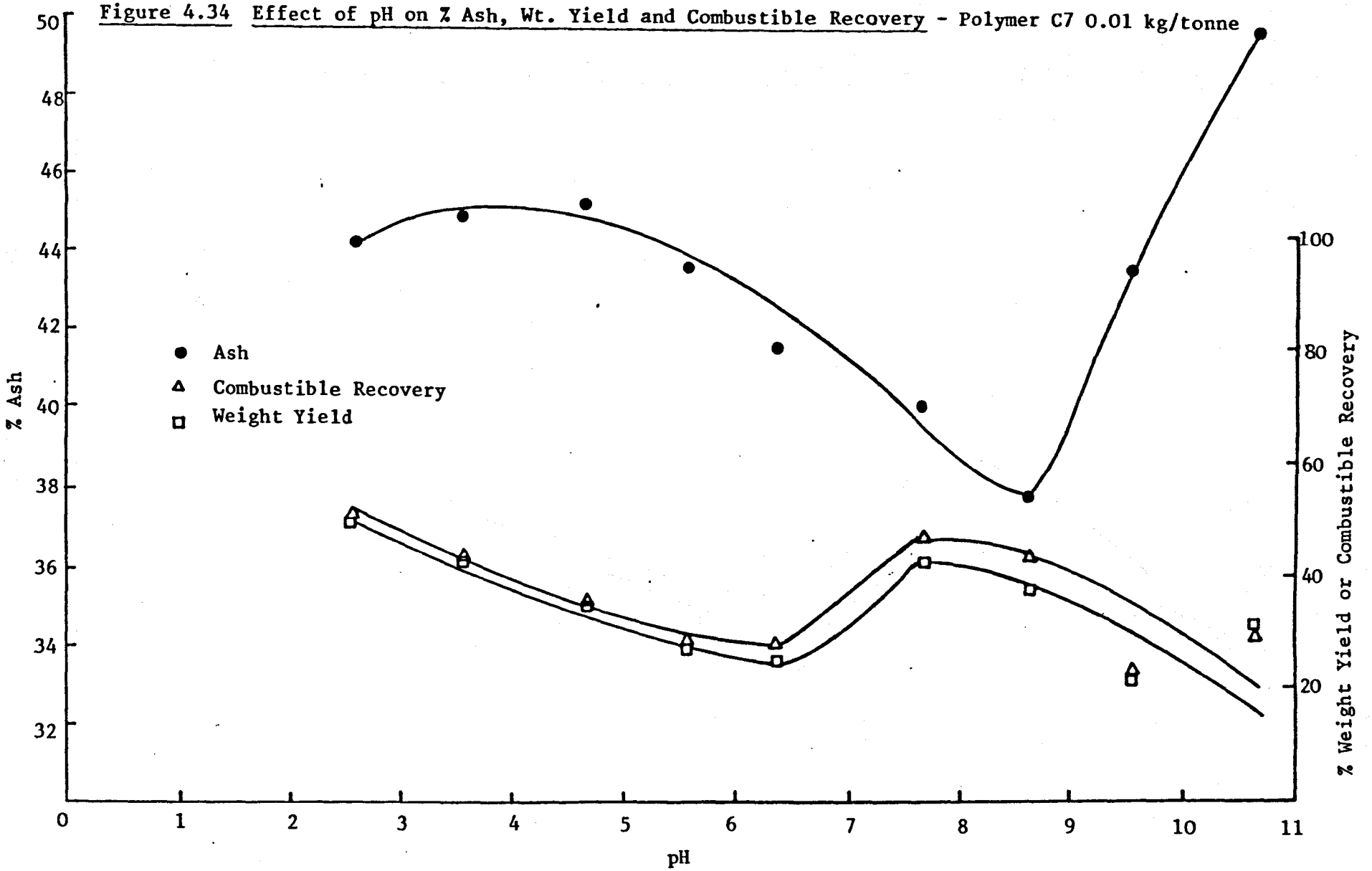
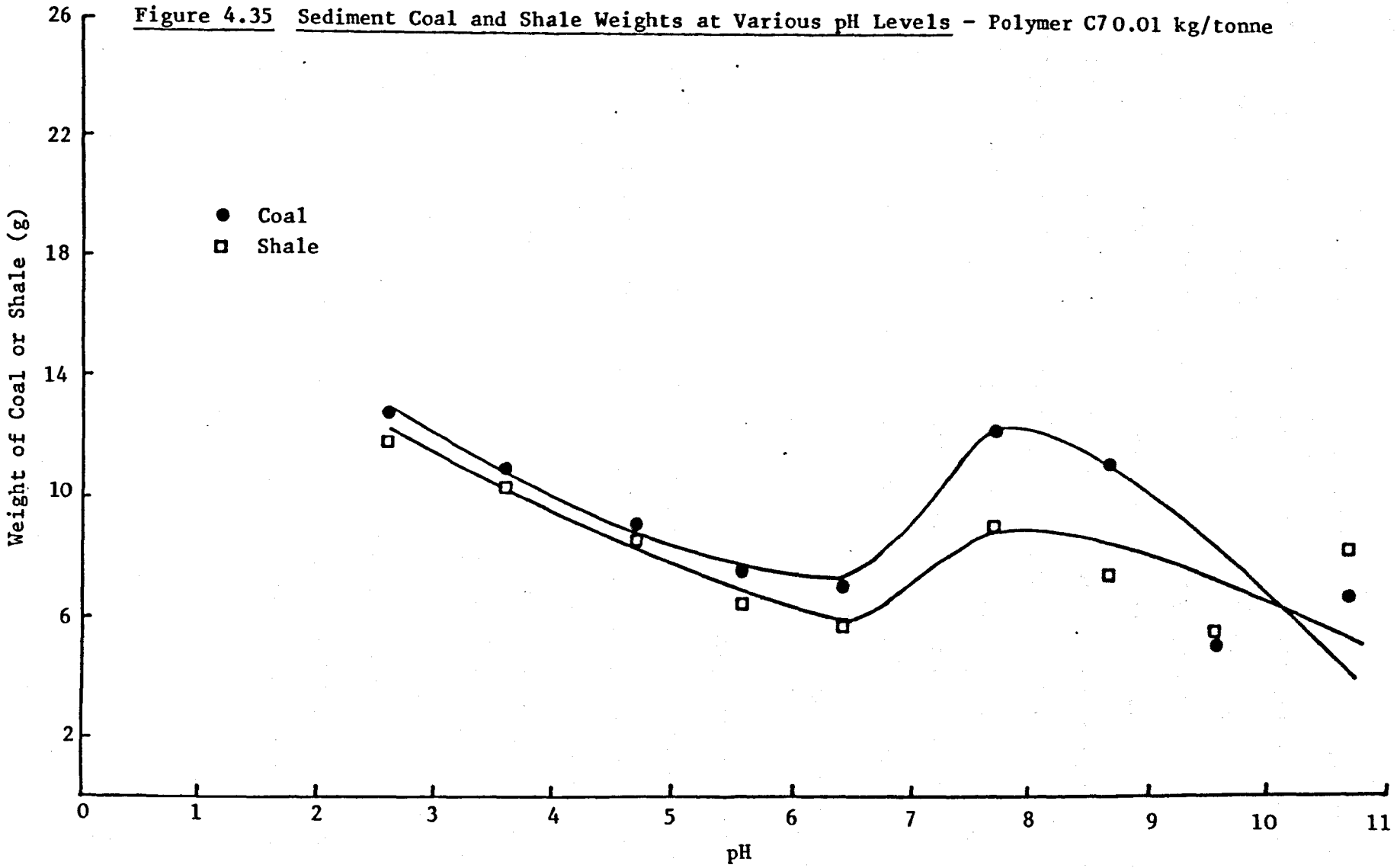


Figure 4.35 Sediment Coal and Shale Weights at Various pH Levels - Polymer C7 0.01 kg/tonne



Considering the results obtained it would appear that negligible selectivity was achieved except perhaps at pH's 7.7 and 8.7. Since the separation was very difficult, any variations in weight yields at low and high pH are probably due to the indiscernable interface produced.

The high positive charge density of this polymer appears to have resulted in adsorption at many points of attachment at low pH. A subsequent flattening of the polymer chains occurred leaving insufficient "loops and tails" for bridging. Again at high pH, shielding of the polymer by hydroxyl ions creates intense repulsion (as shown in Figure 4.38). Between pH 7.7 and 8.7, due to the combined effects of attraction, repulsion and hydrophobic interactions, some selectivity towards the coal is apparent. However, with an ash content of as high as 37.5% and corresponding weight yield and combustible recovery of about 45%, this system is far from selective, and also appears inefficient.

4.4.3 Summary

This study dealing with the effects of pH on selective flocculation has suggested the following:

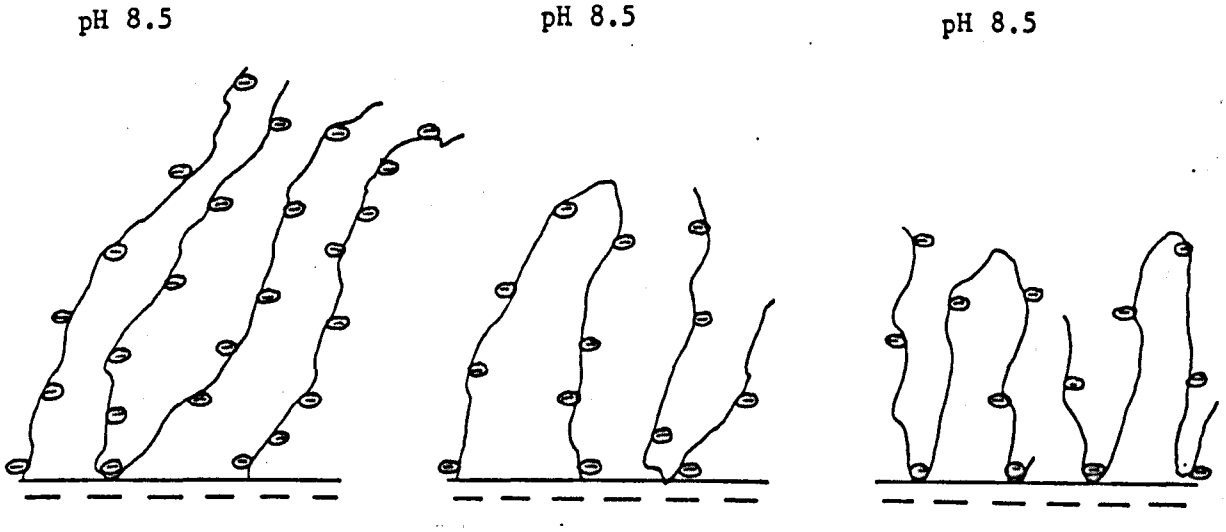
1. Employing polymers of 50% anionic charge density, the pH is a critical parameter, with optimum results being obtained between 6.3 and 6.5. Any variation form this, albeit large or small, will result in a less selective and less efficient system.

2. When employing a non-ionic polymer, a reasonably low ash product is obtained over a wider pH range, although the optimum results for all variables i.e. weight yield, combustible recovery, ash and individual sediment weights are obtained at pH 6.5.

Expanding these two points, different modes of adsorption might be expected at one particular pH depending upon the degree of polymer anionicity. This is shown in Figure 4.39. Thus as the percentage anionic character is decreased, ideal conditions for adsorption and bridging may be achieved at a higher pH and/or over a wider pH range.

3. The percentage cationicity also appeared to be a determining factor. When this was high intense electrostatic attraction resulted in a lack of selectivity and efficiency. A minimal positive charge density however reduced attractive forces and improved conditions for more selective flocculation. However, with all cationic polymers at high pH, shielding of the charge density by hydroxyl ions resulted in a loss of selectivity and efficiency. Optimum pH appeared to be dependent upon cationic character, since the latter affected the degree of polymer-surface/attraction-repulsion forces.

Figure 4.39 Suggested Adsorption of Various Anionic Polymers at Constant pH



In view of the fact that, in the majority of cases, optimum results had been achieved at a pH of approximately 6.5, it was decided to conduct all further testwork at this level.

4.5 EFFECT OF SOLIDS CONCENTRATION

While the tests reported to date were conducted at a solids concentration of 5% (w/v), at the outset, it was realised that optimum conditions would be at a level such that a balance between gangue entrainment and flocculant contact was produced (81). The following section discusses the results of investigations into the effects of variations in the solids concentration. It was not anticipated that these would change with the later employment of the specially prepared polymers.

For the tests, two polymers, a 5% cationic and a non-ionic type were used. On the basis of the earlier work the conditions employed were 0.01 kg/tonne at pH 6.5.

The results are listed in Table 4.2 and are illustrated in Figures 4.40 and 4.41. It can be seen that the original choice of 5% (w/v) was sound in that maximum selectivity i.e. minimum ash, was obtained around this value; corresponding weight yields and combustible recoveries were also acceptable. The figure of 5% (w/v) is typical of that encountered in the froth flotation process and as stated above is a balance between improved probability of contact between particles and the flocculant, and entrainment of shale in the coal flocs. Below the optimum, poor contact results in low weight yields and limited selectivity, whereas above the optimum, shale entrainment leads to

Figure 4.40 Variation of % Ash, Wt. Yield and Combustible Recovery with % Solids Concentration - Polymer C1

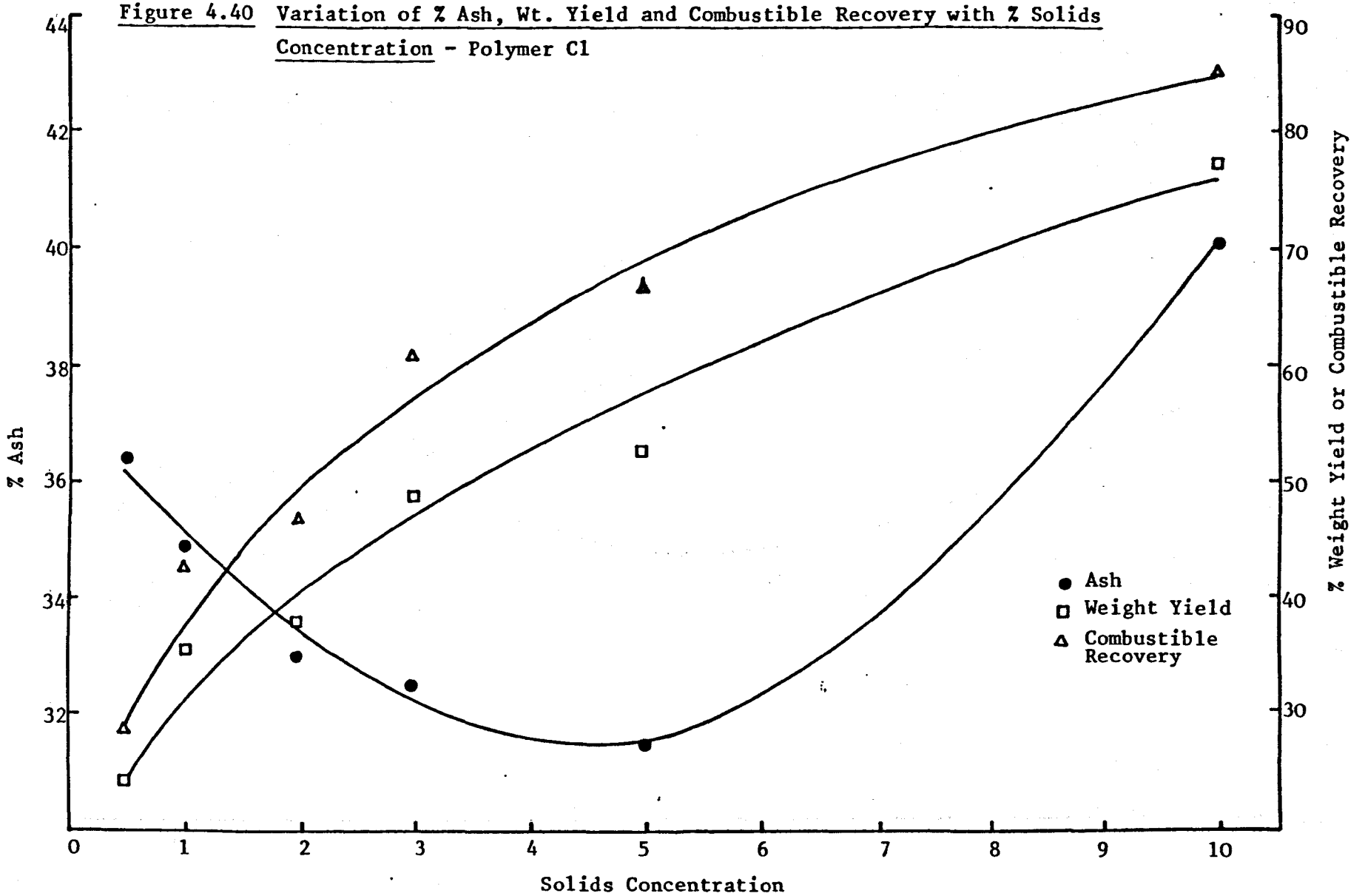
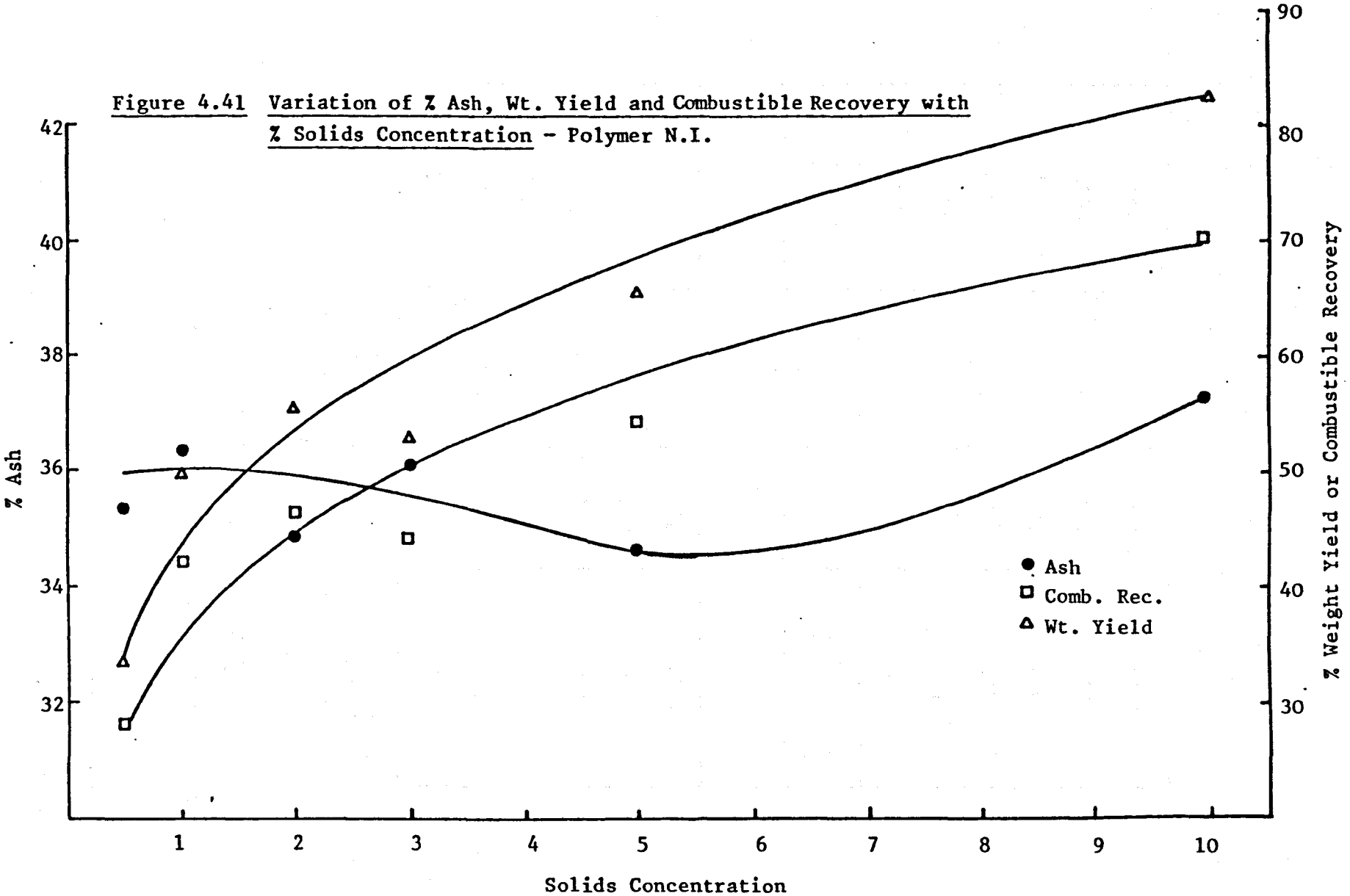


Figure 4.41 Variation of % Ash, Wt. Yield and Combustible Recovery with % Solids Concentration - Polymer N.I.



higher weight yields but much increased ash levels. These results are similar to those found by Abdelrahman (75) in work in the Olifloc process.

Table 4.2 Variation of % Ash, Combustible Recovery and Weight Yield with Solids Concentration

Polymer N.I.

% (w/v) Solid Concentration	% Ash	% Weight Yield	% Combustible Recovery
0.5	35.4	28.0	33.5
1.0	36.4	42.2	49.7
2.0	34.9	46.3	55.8
3.0	36.1	44.3	52.5
5.0	34.7	54.2	65.5
10.0	37.3	70.7	82.1

Polymer C1

% (w/v) Solid Concentration	% Ash	% Weight Yield	% Combustible Recovery
0.5	36.4	24.0	28.3
1.0	34.9	35.2	42.4
2.0	33.0	37.8	46.9
3.0	32.5	48.9	61.1
5.0	31.4	52.4	66.5
10.0	40.1	77.2	85.6

4.6 USE OF A PROMOTER - INITIAL TESTS

It was apparent that there was some selectivity towards the coal and therefore by making its surface more hydrophobic this effect might be expected to be increased. This approach may be likened to the action of a promoter in flotation. Oils with low solubility are widely used. Droplets of the oil dispersed in the pulp adhere to the mineral during conditioning making it more hydrophobic. This process is not spontaneous and intense mechanical agitation is necessary in order to produce sufficient force to spread the oil. Common collectors for coal flotation include diesel oil and creosote. These were chosen for use in selective flocculation testwork, along with oleic acid which had been used with some success in a previous project within the University (75) as a pre-conditioner for selective agglomeration. It is also a common collector for non-metallic minerals, such as fluorite and barite.

The tests were conducted as described in section 4.4.1, except that the promoter was added prior to the dispersion stage and pH adjustment. The polymer used was C7, a 50% cationic polymer, which without a conditioning reagent had produced a sediment ash of almost 42% (at pH 6.4), indicating only minimal selective action. Promoter additions of between 0.5 to 5 kg/tonne were used with a constant polymer dosage of 0.01 kg/tonne. The results are given in Appendix 6 and shown graphically in Figures 4.42 to 4.47.

Figure 4.42 indicates reductions in the ash content with increasing oleic acid addition, combined with enhanced weight yields and combustible recoveries. This would suggest that both the

selectivity and efficiency of the separation are improved by the addition. Figure 4.43 shows a progressive rise in coal sediment weights over the dosage range, while shale weights remain similar throughout. Hence the effect of increased dosages of oleic acid generally reflects its action toward coal. It was noted that directly following oleic acid addition coal particles were agglomerated. This suggests that the presence of oleic acid in the system reduces repulsion forces between coal particles thus allowing them to agglomerate, initiating a separation. Oleic acid, $C_{17}H_{33}COOH$, is most probably adsorbed as the anion since ionisation occurs over a wide pH range (116). It is adsorbed at the surface of alkaline earth minerals with the formation of a film of insoluble oleate and is also known to chemisorb on fluorite (116). The calcium and magnesium ions which are present in the water may therefore be attracted to polar coal surface sites and thus facilitate the adsorption of oleic acid oriented with non-polar chains outward. Physical adsorption, with polar groups oriented outward is also a possibility. Thus polar groups on the surface may oppose the adsorption of non-polar chains without preventing it. The overall effect is likely to be an increase in coal hydrophobicity which leads to attraction between adjacent coal particles via hydrophobic bonding. A reduction in coal surface charge may result from some shielding of the surface by the hydrocarbon chains; this could lead to coagulation type attractions and may prevent the strong electrostatic polymer adsorption which was postulated previously (section 4.4.2(e)). This would produce more favourable conditions for bridging in the form of available "loops and tails". However without additional testwork

Figure 4.42 Variation of % Ash, Wt. Yield and Combustible Recovery with Oleic Acid Addition - Polymer C7

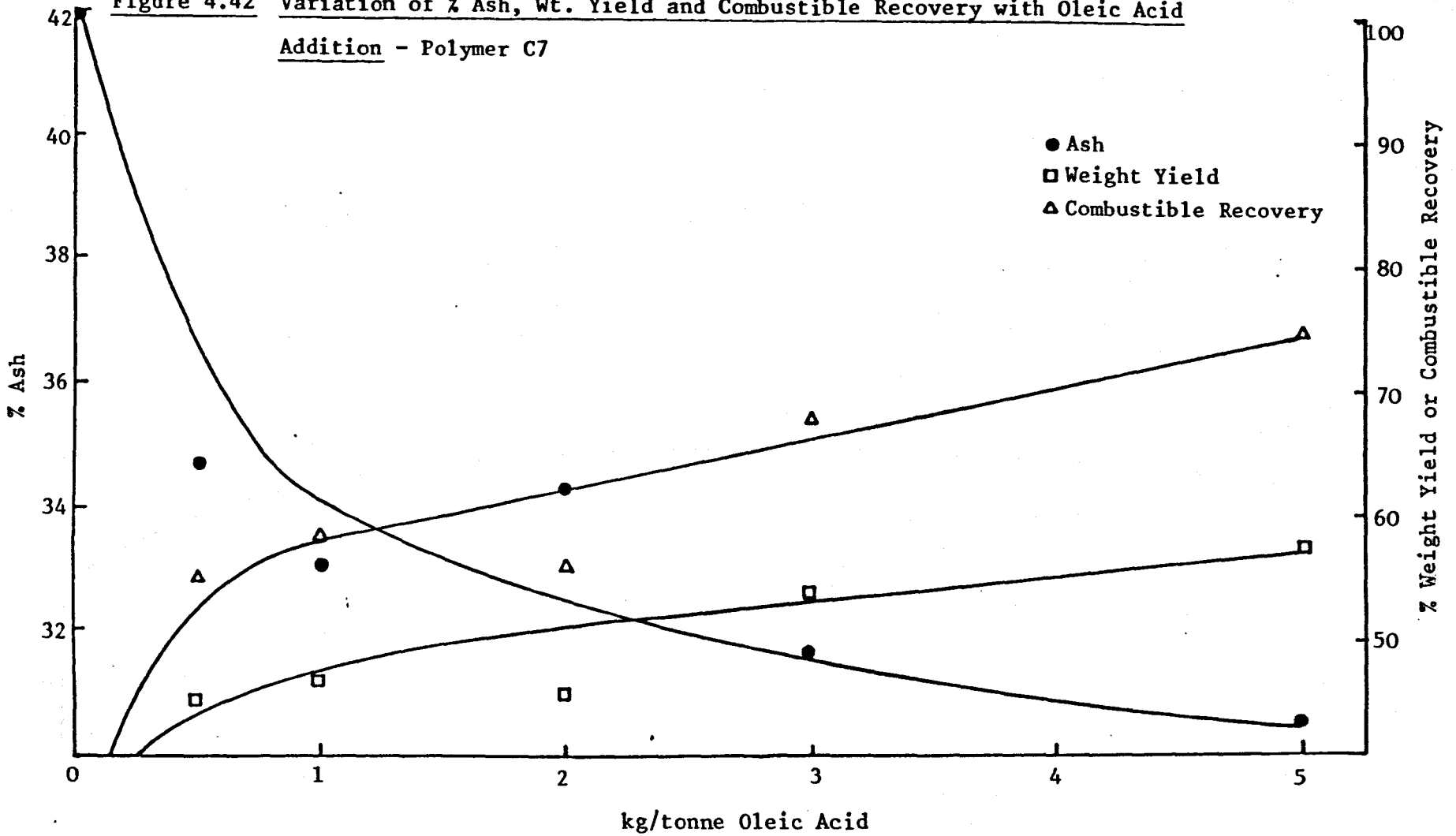
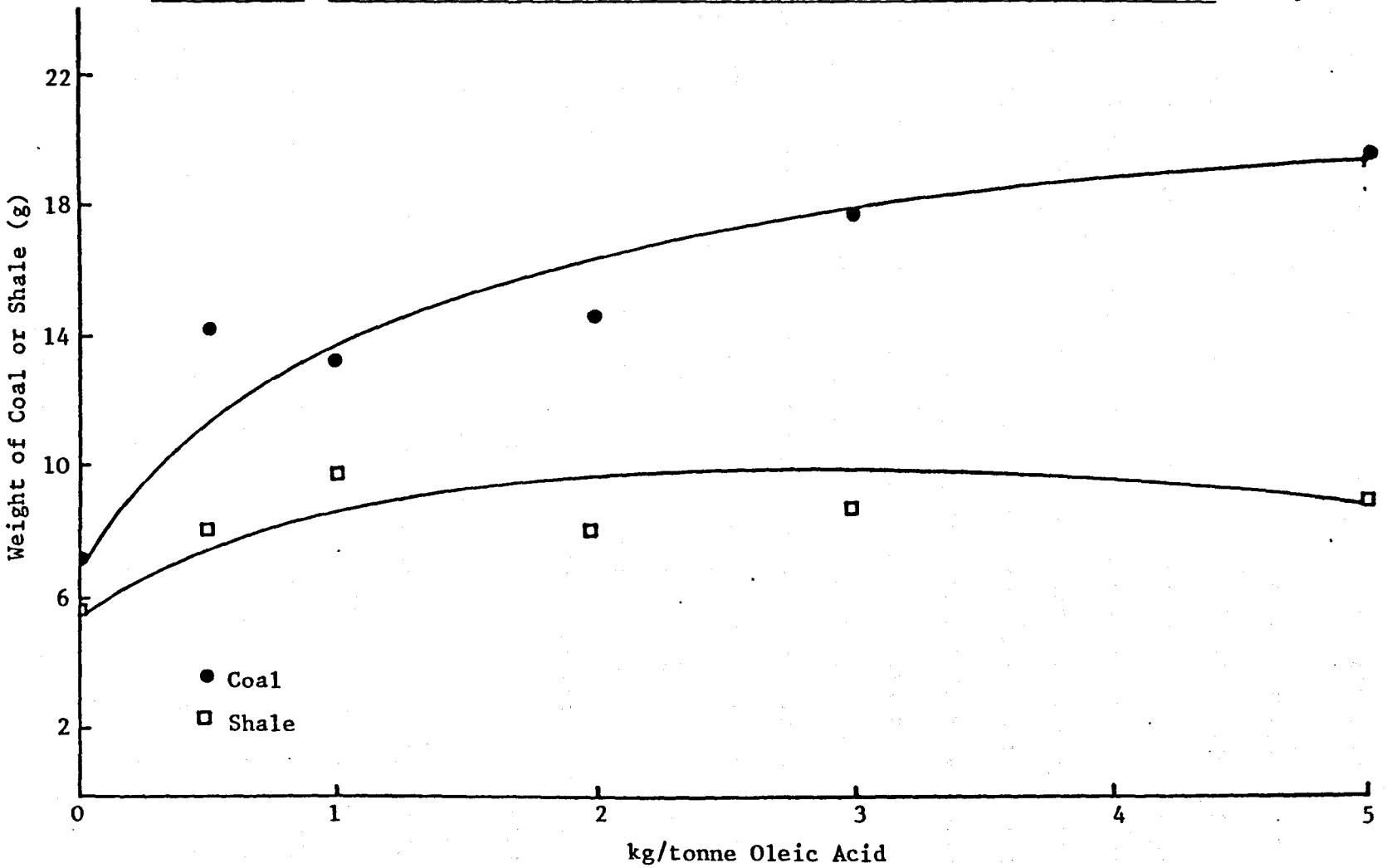


Figure 4.43 Sediment Coal and Shale Weights with Various Oleic Acid Additions - Polymer C7



it is difficult to ascertain whether it is mainly the action of the oleic acid alone, or this in conjunction with polymer flocculation which leads to the increase in selectivity and efficiency.

For the creosote addition, Figure 4.44 shows a decrease in ash content at low dosage levels i.e. 0.5 to 1 kg/tonne, together with a sharp rise of about 30% in weight yields and combustible recoveries. This is followed by a gradual increase in ash content with corresponding decreases in the other two variables. As seen in Figure 4.45, coal sediment weights are seen to increase considerably up to a dosage of 0.5 kg/tonne creosote; above this level however they decline slowly. A gradual increase in shale sediment weight is noted over the whole creosote dosage range. Hence at levels up to 0.5 kg/tonne, the addition of creosote considerably improves both the selectivity and efficiency of flocculation. It is suggested that this is the result of some masking of the negative surface sites on coal which, before promoter addition, resulted in strong electrostatic polymer adsorption and subsequent loss of flocculating ability. Thus hydrophobic interactions may be occurring in addition to reduced electrostatic attractions, overall providing an improved situation for bridging; however shale entrainment is also enhanced. Above a level of 0.5 kg/tonne, bonding sites are masked still further resulting in reductions in selective coal flocculation. The marginal increases in shale sediment weights, also noted above this level, may be attributed to increased polymer adsorption at the shale surface and thus to consequential increased flocculation.

For the diesel oil, Figure 4.46 indicates a sharp decrease in ash content with dosages up to 1 kg/tonne. However, further increases produced only slight improvements in ash content, weight yield and combustible recovery. Figure 4.47 illustrates a

Figure 4.44 Variation of % Ash, Wt. Yield and Combustible Recovery with Creosote Addition - Polymer C7

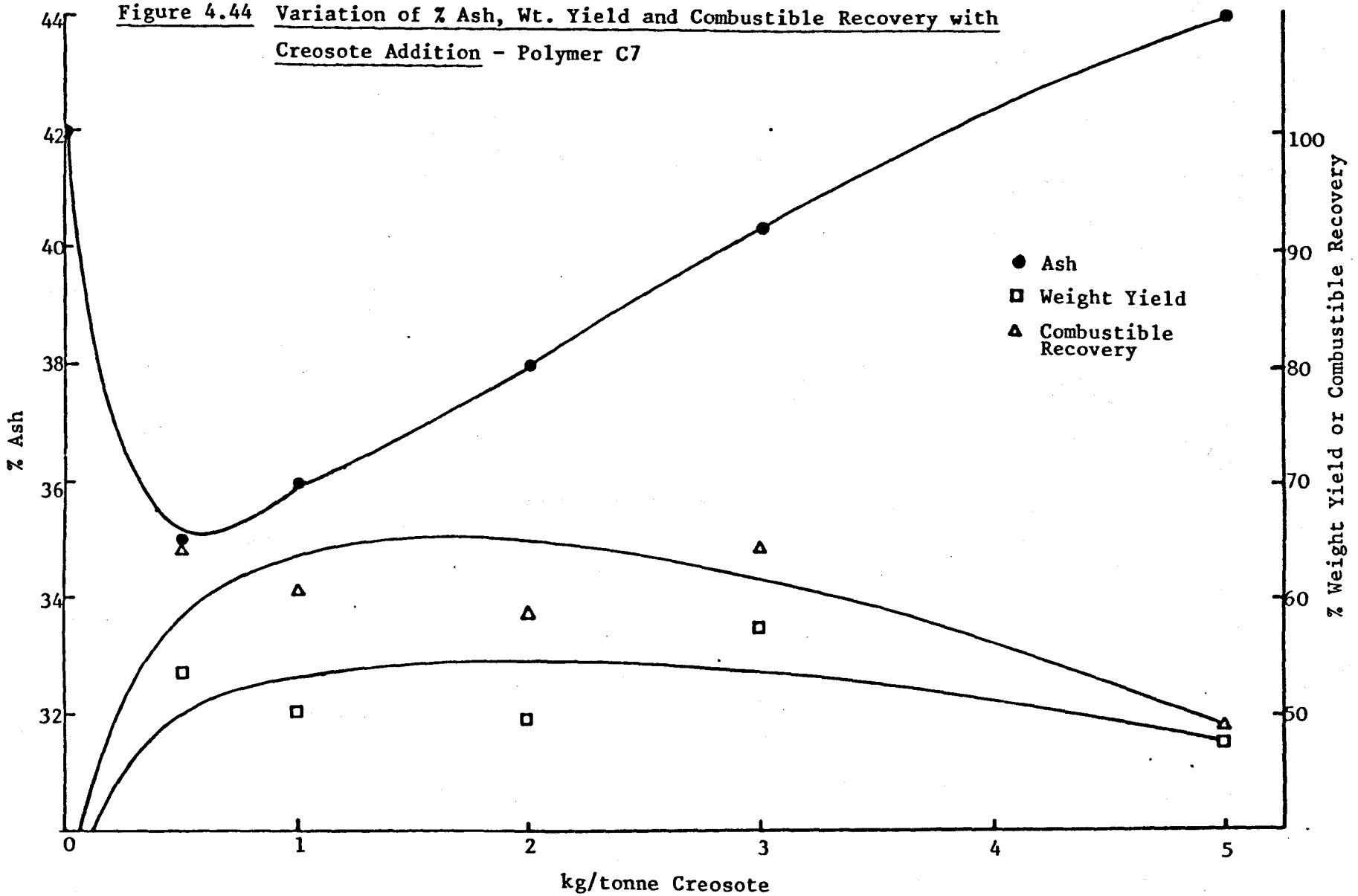


Figure 4.45 Sediment Coal and Shale Weights with Various Creosote Additions - Polymer C7

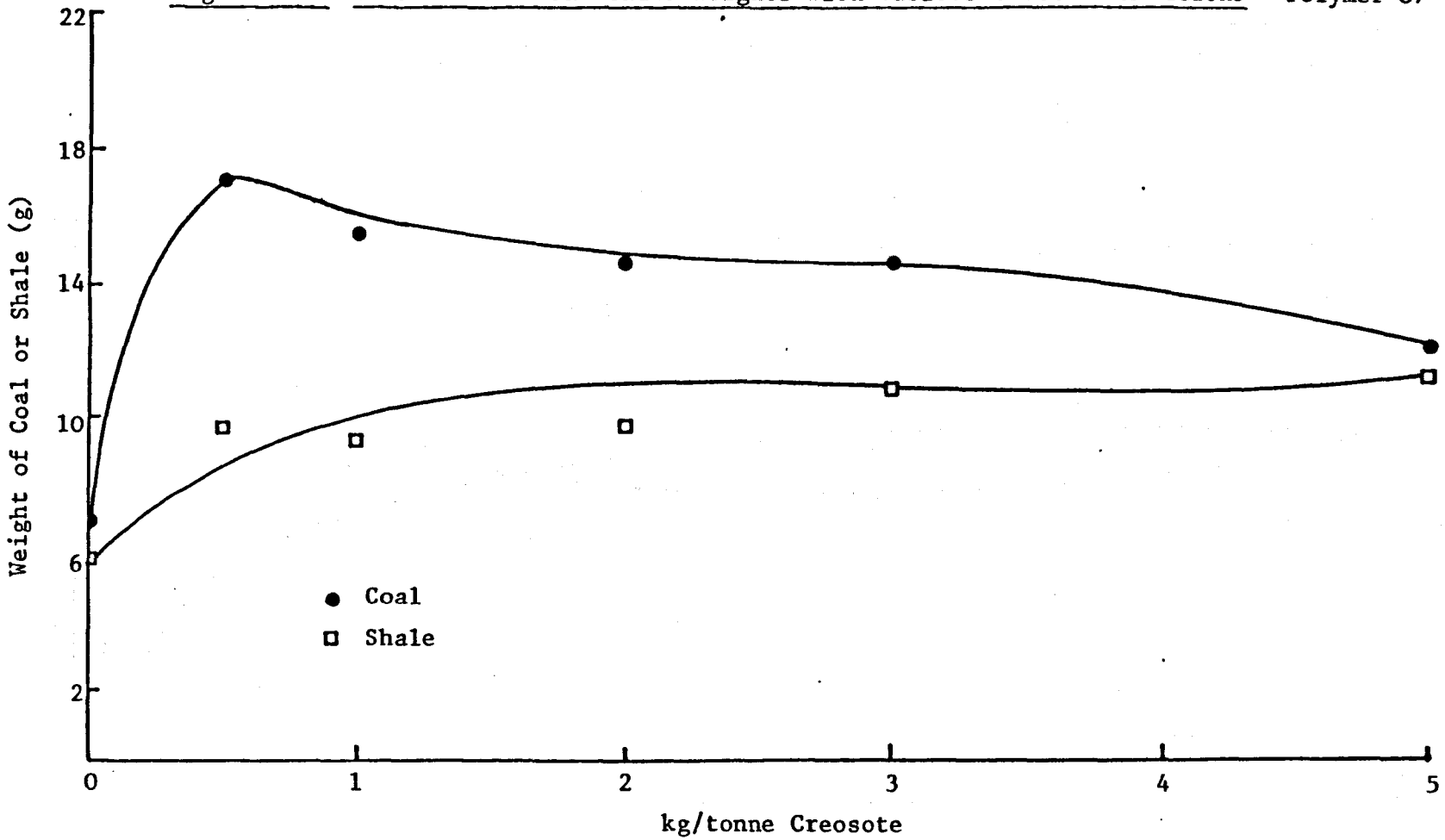


Figure 4.46 Variation of % Ash, Wt. Yield and Combustible Recovery with Diesel Oil Addition - Polymer C7

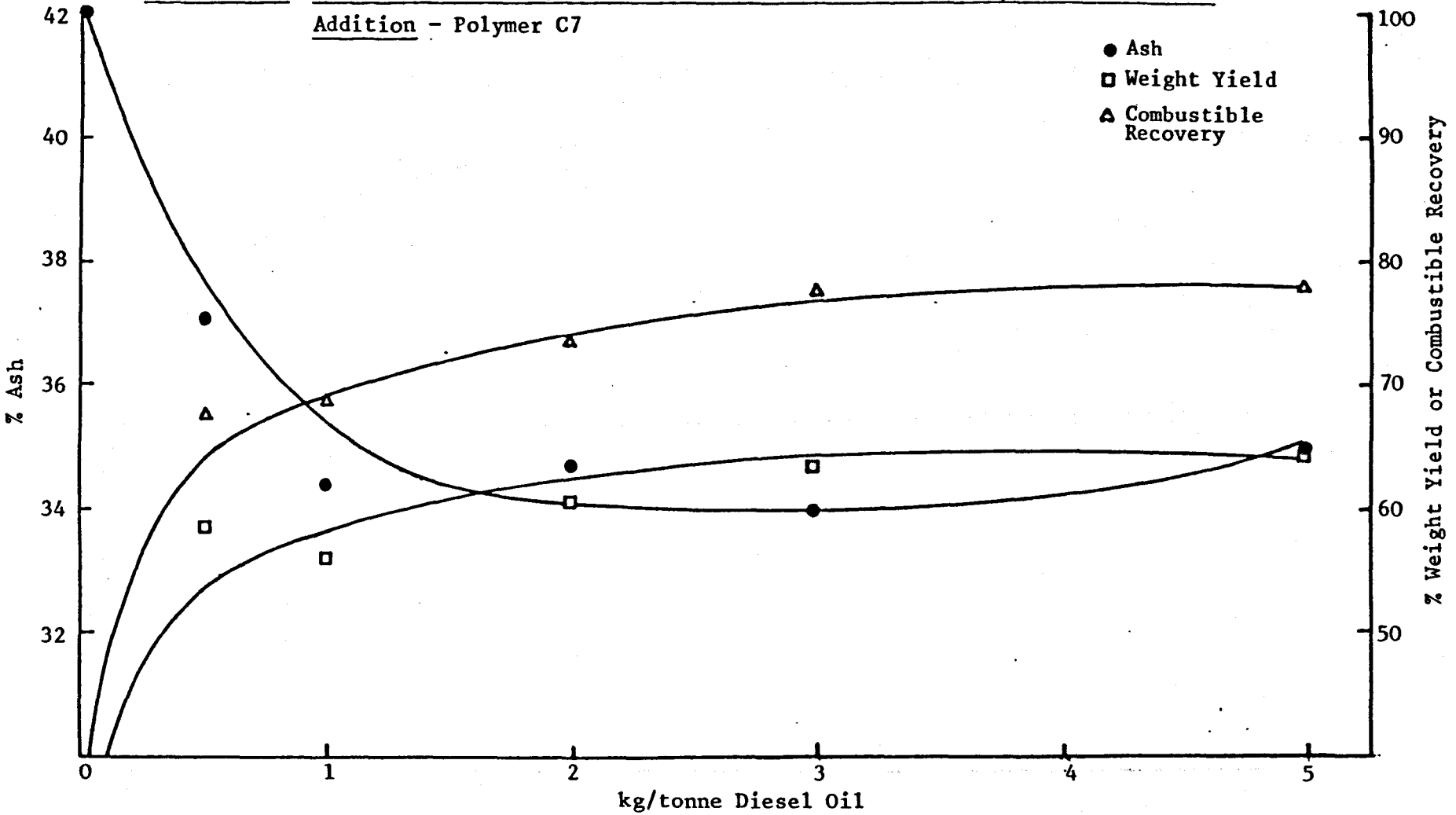
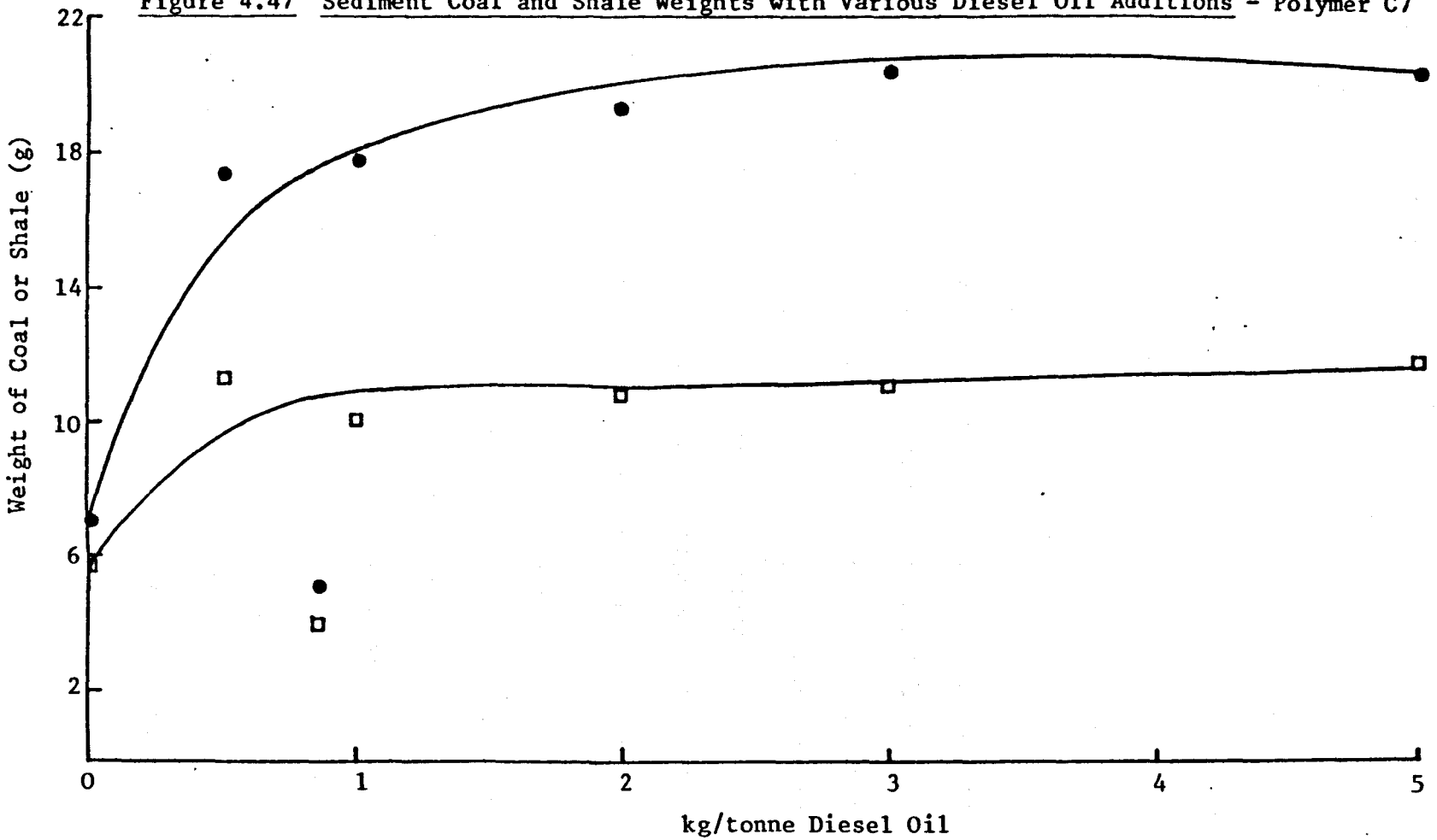


Figure 4.47 Sediment Coal and Shale Weights with Various Diesel Oil Additions - Polymer C7



general increase in both sediment coal and shale weights over the dosage range, with those of coal increasing more than those of shale. Thus, the indications are that the diesel oil increased the hydrophobicity of the coal surface, allowing more selective polymer adsorption and flocculation; however this appeared to increase shale pickup. Hence although ash contents remained similar, weight yields were increasing. Diesel oil droplets have been reported as being both negatively charged and neutral (75) but whatever their nature they will have an attraction for the coal surface, due to physical adsorption, which will be followed by spreading during the dispersion period.

The conclusions from this initial study are that both the selectivity and efficiency of flocculation may be improved with the addition of certain "surfactant type" reagents to a system. Ash contents however remain relatively high and flocs comparatively weak. It was clear that further work was required in this area in order to quantify promoter effects when employing various other polymer types. Section 5.3 describes a more detailed study in this area.

CHAPTER 5

SELECTION OF NEW POLYMER SAMPLES

The results of the initial testwork had indicated that various types of polyacrylamide polymers could be utilised with varying degrees of success for the flocculation of both coal and shale. Similarly the same polymers were capable, at near neutral pH, of selectively flocculating coal from a mixed coal/shale slurry. Further tests had shown that a 5% w/v solids concentration provided optimum conditions and that pre-treatment with a "surfactant type" reagent could improve the selectivity of the system. However, due to the wide ranging ionic characters and molecular weights of the polymers used, it had not been possible to determine their precise influences on either conventional or selective flocculation It was therefore envisaged that a range of polymers with constant percentage ionic character, but having various molecular weights, would remove this uncertainty. Consequently, a range of six, 50% anionic polymers, and six essentially non-ionic polymers were obtained. Details of these are given in Table 5.1.

5.1 SETTLING TESTS

In order to determine the effectiveness of each polymer it was decided to repeat the initial settling tests on separate coal and shale samples. In the initial testwork, a lower calgon dosage, (0.08 kg/tonne), had been employed in the settling tests compared with that used in the selective flocculation work (0.5 kg/tonne).

Table 5.1 New Polymer Samples

Polymer Identification	Molecular Weight	Ionic Character
A	1.8×10^6	Non-Ionic
B	3.6×10^6	Non-Ionic
C	6.2×10^6	Non-Ionic
D	9.3×10^6	Non-Ionic
E	11.5×10^6	Non-Ionic
F	18.2×10^6	Non-Ionic
G	5.0×10^6	50% Anionic
H	6.9×10^6	50% Anionic
I	8.2×10^6	50% Anionic
J	10.2×10^6	50% Anionic
K	12.0×10^6	50% Anionic
L	20.0×10^6	50% Anionic

In order to establish the effects of dispersant dosage on flocculation, and later, upon selective flocculation, it was decided to conduct the settling tests at both of these levels.

5.1.1 Experimental

Fifty grams of coal or shale were added to 0.8ℓ of deionised water* containing Mg^{2+} (0.09 kg/tonne), Ca^{2+} (0.1 kg/tonne) and the required calgon dosage. This was mixed at 2000 rpm** for 2 mins and the pH adjusted to ≃ 6.5 prior to transfer to the settling vessel. The required volume of polymer was diluted to 200 cm^3 and added to the settling vessel which was then inverted four times. The time for the interface to fall 10 cm was recorded. Polymer dosage levels of between 0.01 and 0.3 kg/tonne were used. The results of these tests are given in Appendix 7; typical results are presented graphically in Figures 5.1 to 5.4.

5.1.2 Discussion of Results

It is clear that the settling velocities of both coal and shale were increased by the addition of the polymer. Several points are however apparent:

(i) Molecular weights

All graphs show that increasing polymer molecular weight generally enhances settling velocities. This would tend to lend support to the suggestion in section 4.1.2 that the large peaks

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* Deionised water was utilised due to its ease of production. Excessive quantities were necessary in the tests being conducted, with the result that distillation became impractical.

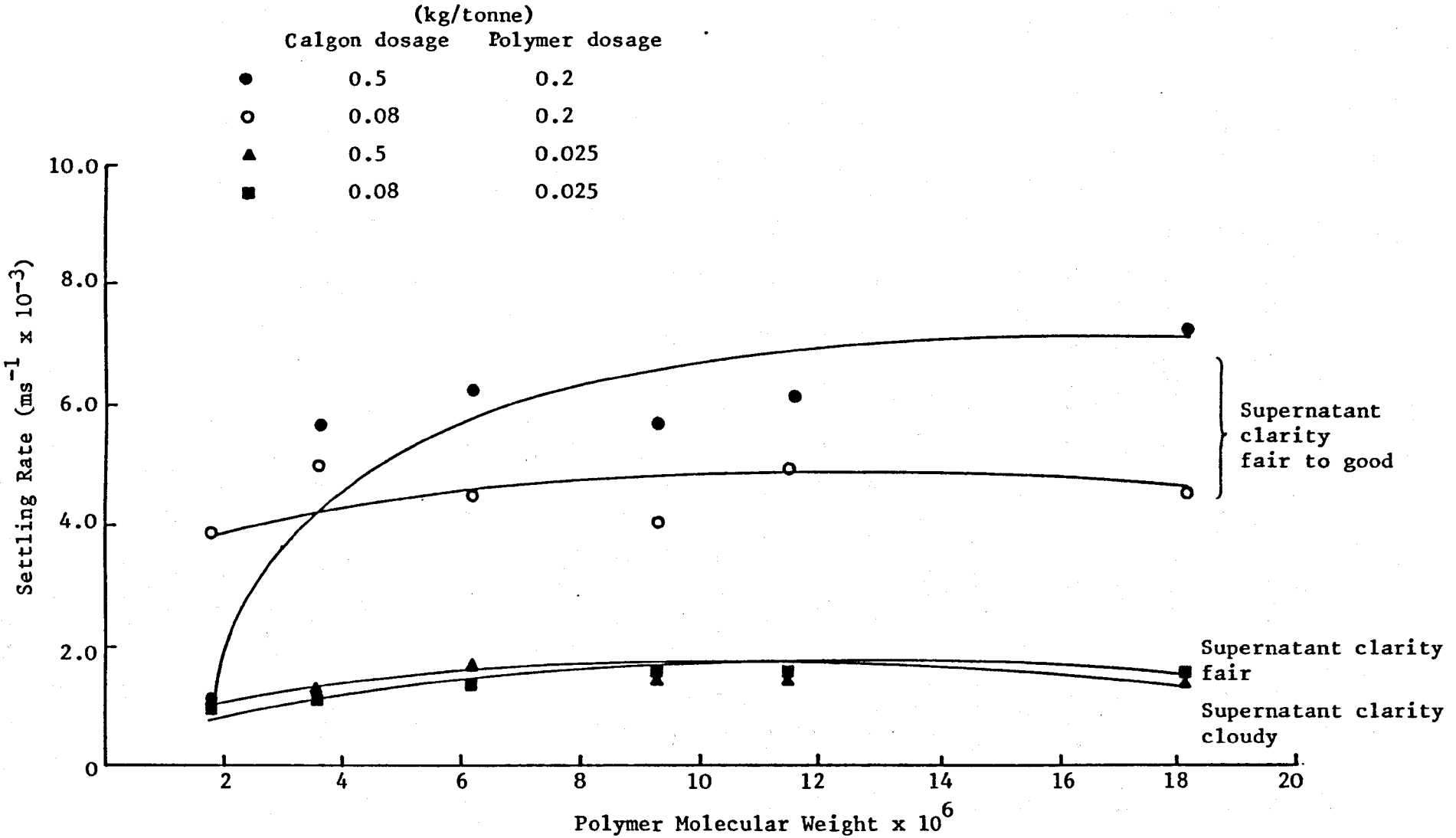
** A high speed blender was used due to the non-availability of the previously used stirring system.

observed in the previous settling tests were mainly the result of variations in polymer molecular weight.

(ii) Figure 5.1 - Settling velocities of shale with non-ionic polymers.

For this system the highest settling rates were achieved using a combination of high dispersant and high polymer dosage. Significant settling rates were also obtained with a high polymer addition coupled with the lower dispersant dosage. At the lower polymer dosages, regardless of dispersant concentration, similar low settling rates were obtained, but since the lower calgon dosage produced a clearer supernatant, this indicated an increased degree of flocculation. Thus it would appear that, even in the presence of large quantities of dispersant, at higher polymer dosage levels large flocs are formed. Therefore although the predicted increase in shale zeta potential at the higher calgon dosage (79) might be expected to improve dispersion, hydrogen bonding mechanisms are able to overcome this and provide favourable conditions for bridging, particularly at a high polymer dosage level. The observation that the highest settling velocities were obtained at a high calgon dosage coupled with a high polymer addition may be because of slightly improved bridging properties, i.e. due to some increase in polymer/surface repulsion at high calgon dosage, an increase in polymer extension may result since, as stated previously the non-ionic polymers inevitably have some anionic character. If the calgon dosage had been further increased, flocculation may have eventually been inhibited due either to the inability of polymer adsorption mechanisms to overcome the high

Figure 5.1 Settling Rates of Shale with Non-Ionic Polymers



zeta potential or polymer extension being unable to overcome the tendency of the highly charged particles to remain apart.

(iii) Figure 5.2 - Settling velocities of coal with non-ionic polymers.

As expected, an increase in settling velocities is achieved on increasing polymer dosage; this has been previously discussed in section 4.1.2 and occurs almost regardless of dispersant dosage. It is suggested that the presence of calgon influences the coal zeta potential, and consequent polymer adsorption, to a much lesser extent than in the case of the shale.

(iv) Figure 5.3 - Settling velocities of shale with 50% anionic polymers.

Regardless of polymer dosage, settling velocities are considerably reduced when large quantities of dispersant are added. This is despite their expansion into solution which may have been expected to increase their bridging ability (117). Previous work (79) has indicated that dispersant dosage influences the zeta potentials of calcite and alumina; a similar concept may also be envisaged for shale. In addition, Kuzkin and Nebera (32) have suggested that an anionic flocculant will not adsorb on a negatively charged mineral surface having a zeta potential above a certain value, this value being dependent on the anionicity of the flocculant. The combined effect of these two proposals is illustrated in Figure 5.5. In the initial settling tests using a low dispersant dosage (section 4.1.3) the adsorption of a 100% anionic polymer was inhibited. This indicates that, as suggested above, it is a combination of both shale zeta potential and polymer anionicity

Figure 5.2 Settling Rates of Coal with Non-Ionic Polymers

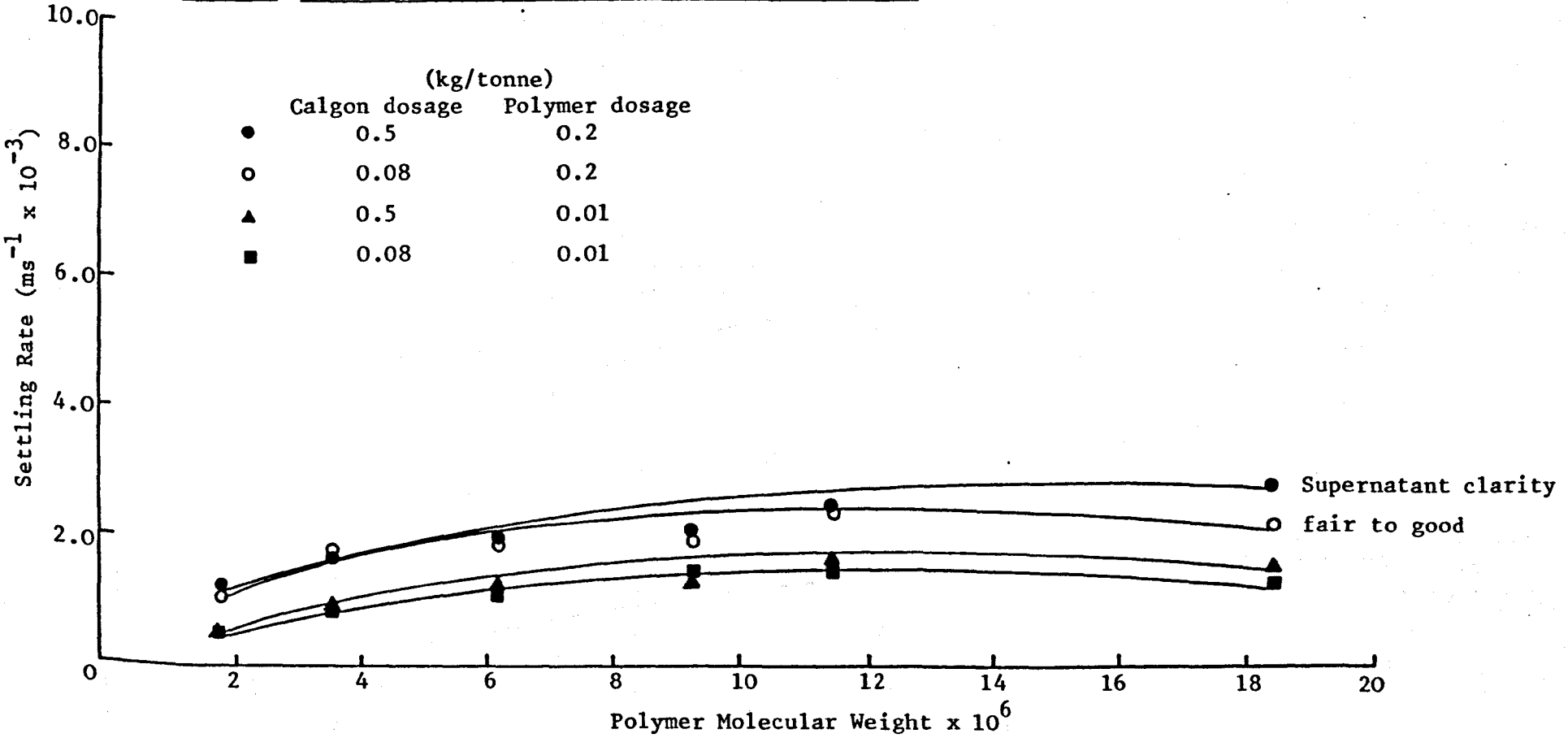


Figure 5.3 Settling Rates of Shale with 50% Anionic Polymers

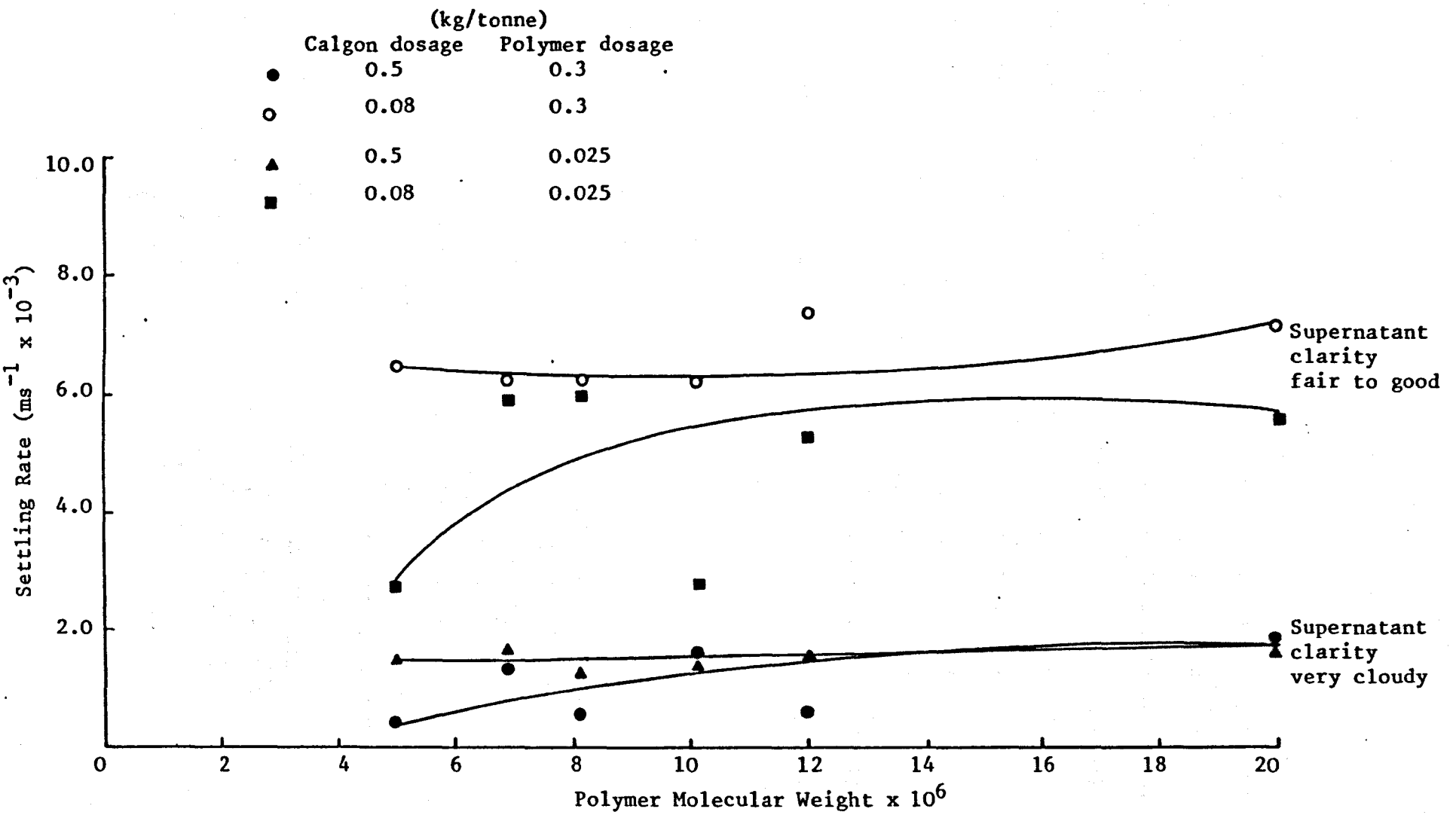
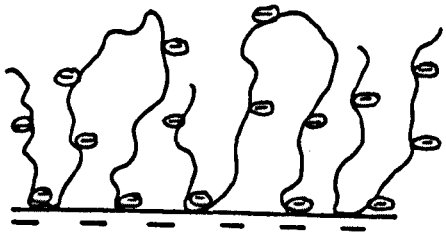


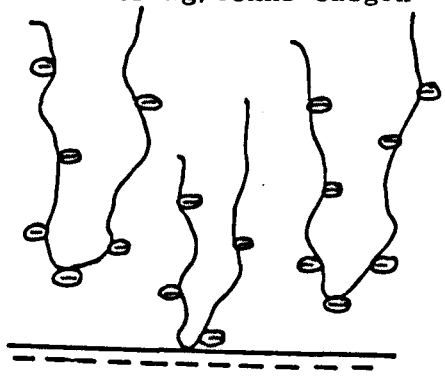
Figure 5.5 Effect of calgon dosage on the flocculation of Shale using 50% anionic polymers

0.08 kg/tonne calgon



Low zeta potential but high charge on extended polymer results in surface/polymer repulsions and produces "loops and tails" for bridging. Good settling rates are achieved.

0.5 kg/tonne calgon



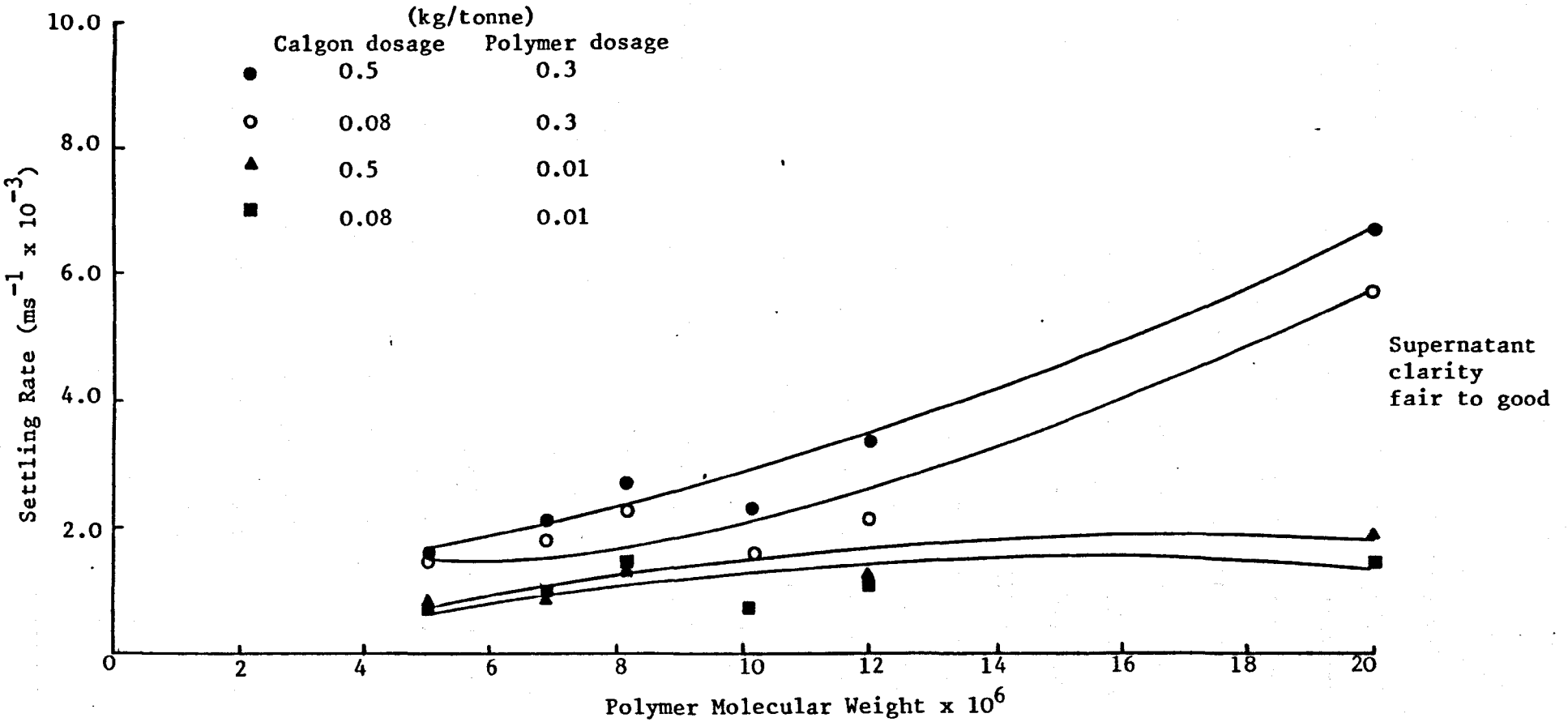
Higher zeta potential results in electrostatic repulsion between shale particles. Due to excess electrostatic repulsion between polymer and shale surface adsorption is inhibited. Degree of flocculation, and hence settling rates, greatly reduced.

which determines the degree of polymer adsorption and thus the effectiveness of shale flocculation.

v) Figure 5.4 - Settling velocities of coal with 50% anionic polymers

Again coal settling velocities are only marginally affected by an increase in calgon dosage. As expected however they do increase with a higher polymer dosage. This would lend increased support to the suggestion that calgon does not interact with the coal surface and as such exerts little influence on its zeta potential (as initially suggested in section 4.3.6) or on polymer adsorption.

Figure 5.4 Settling Rates of Coal with 50% Anionic Polymers



5.1.3 Summary

The main conclusions which may be drawn from these results are:

1. Settling velocities of coal and shale generally increase with an increase in polymer molecular weight; the increase appears to be more pronounced with anionic polymers.

2. Ionic character and dosage of the polymer, and dispersant addition, affect the settling velocities of shale for reasons based on a combination of both polymer anionicity (and thus solution expansion) and shale zeta potential. These are such that at:

(i) Low calgon dosage and low polymer dosage - Non-ionics settle shale slowly due to the small size of floc produced; anionics having greater expansion in solution possess increased flocculating ability.

(ii) Low calgon dosage and high polymer dosage - The performance of both polymers is increased due to the larger floc size, however that of the anionics is superior because of the additional influence of its extension into solution.

(iii) High calgon dosage and low polymer dosage - Similar low settling velocities are obtained with both polymer types. Non-ionics again produce smaller flocs but settling rates are little affected by this increase in calgon dosage; supernatant clarities are however decreased. Due to an increase in shale zeta potential combined with the anionicity of the polymer, long range repulsive forces oppose adsorption of the anionic polymers, at all levels; this reduces settling velocities in comparison with those achieved at the low calgon dosage.

(iv) High calgon dosage and high polymer dosage - Larger flocs are produced with the non-ionics leading to enhanced settling velocities over those obtained at the lower polymer level. This suggests that polymer adsorption mechanisms are little affected by any change in zeta potential, with hydrogen bonding mechanisms, as opposed to electrostatic interactions, playing a major role. However, long range electrostatic repulsions oppose anionic polymer adsorption and thus settling velocities are low.

3. The dispersant dosage has little effect on coal settling velocities, provided polymer dosage remains similar.

4. Settling velocities of coal using both classes of polymer are similar, except at a high dosage of the highest molecular weight 50% anionic polymer; this may be a reflection of its extended configuration.

On the basis of the findings from the earlier selective flocculation trials, it is appreciated that it is not realistic to speculate, other than in a negative manner, on which component will be flocculated in a mixed slurry. However, dispersant dosage is, in all probability a major contributing factor both to the selectivity and efficiency. This proposal is investigated in the following section.

5.2 SELECTIVE FLOCCULATION

5.2.1 Experimental

Twenty five grams each of coal and shale were dispersed at 2000 r.p.m. in 1 litre of deionised water which contained Mg^{2+} (0.09 kg/tonne), Ca^{2+} (0.1 kg/tonne) and calgon (0.08 or 0.5 kg/tonne). The pH was adjusted to ≃ 6.5 and flocculant (0.01 kg/tonne or 0.025 kg/tonne) added over a period of 1 minute while stirring at 350 r.p.m. in the separating vessel. As in previous tests, 5 minutes was allowed to effect a separation. Both sediment and supernatant were then dried, weighed and ashed in duplicate (104). Weight yields, combustible recoveries and coal and shale sediment weights were calculated as before.

The results of all the tests conducted are shown in Tables 5.2 to 5.17 and are represented graphically in Figures 5.6 to 5.15.

5.2.2 Discussion of Results

(i) Non-Ionic Polymers

A study of Tables 5.2 and 5.3 indicates the following points

i(a) The main effect is undoubtedly that of dispersant dosage, with higher levels of calgon resulting in seemingly increased dispersion of both coal and shale species. The coal/shale ratio is approximately 3:2 at low calgon dosage increasing to 2:1 at the higher dispersant level.

i(b) Coal and shale sediment weights are increased slightly with an increase in polymer addition; this applies at both calgon dosage levels.

Table 5.2 Sediment Coal and Shale Weights at Low Dispersant Dosage - Non-Ionic Polymers

Polymer	0.01 kg/tonne polymer		0.025 kg/tonne polymer	
	Wt. of Coal in sediment	Wt. of Shale in sediment	Wt. of Coal in sediment	Wt. of Shale in sediment
A	21.7	14.7	22.9	15.6
B	21.8	14.9	22.1	15.9
C	21.6	13.2	21.9	15.3
D	21.9	13.9	22.3	14.8
E	20.6	13.0	22.3	14.6
F	21.1	14.1	22.4	13.7

Table 5.3 Sediment Coal and Shale Weights at High Dispersant Dosage - Non-Ionic Polymers

Polymer	0.01 kg/tonne polymer		0.025 kg/tonne polymer	
	Wt. of Coal in sediment	Wt. of Shale in sediment	Wt. of Coal in sediment	Wt. of Shale in sediment
A	17.8	9.7	18.7	9.8
B	15.2	7.9	18.2	9.3
C	16.2	8.7	18.2	10.1
D	15.7	8.6	18.2	9.8
E	17.0	9.2	17.5	9.7
F	17.0	8.0	15.9	8.6

Table 5.4 Sediment % Ash at Low Dispersant Dosage - Non-Ionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
A	37.7	38.2
B	38.2	39.3
C	36.1	38.6
D	36.7	37.6
E	36.6	37.5
F	37.3	36.1

Table 5.5 Sediment % Ash at High Dispersant Dosage - Non-Ionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
A	33.9	33.0
B	33.1	32.5
C	33.6	34.2
D	33.9	33.7
E	33.6	34.3
F	31.2	33.6

Table 5.6 Weight Yields at Low Dispersant Dosage - Non-Ionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
A	72.4	77.0
B	73.4	76.0
C	69.6	74.4
D	71.6	74.2
E	67.2	73.8
F	71.6	72.2

Table 5.7 Weight Yields at High Dispersant Dosage - Non-Ionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
A	55.0	57.0
B	46.2	55.0
C	49.8	56.6
D	48.6	56.0
E	52.4	54.4
F	50.0	49.0

Table 5.8 Combustible Recoveries at Low Dispersant Dosage - Non-Ionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
A	83.5	88.1
B	84.0	85.4
C	82.4	84.6
D	83.9	85.7
E	78.9	85.4
F	83.1	77.9

Table 5.9 Combustible Recoveries at High Dispersant Dosage - Non-Ionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
A	67.3	70.7
B	57.2	68.8
C	61.2	68.7
D	59.5	68.8
E	64.4	66.2
F	63.7	60.3

Figure 5.6 Sediment Coal and Shale Weights at Low Dispersant Dosage - Non-Ionic Polymers

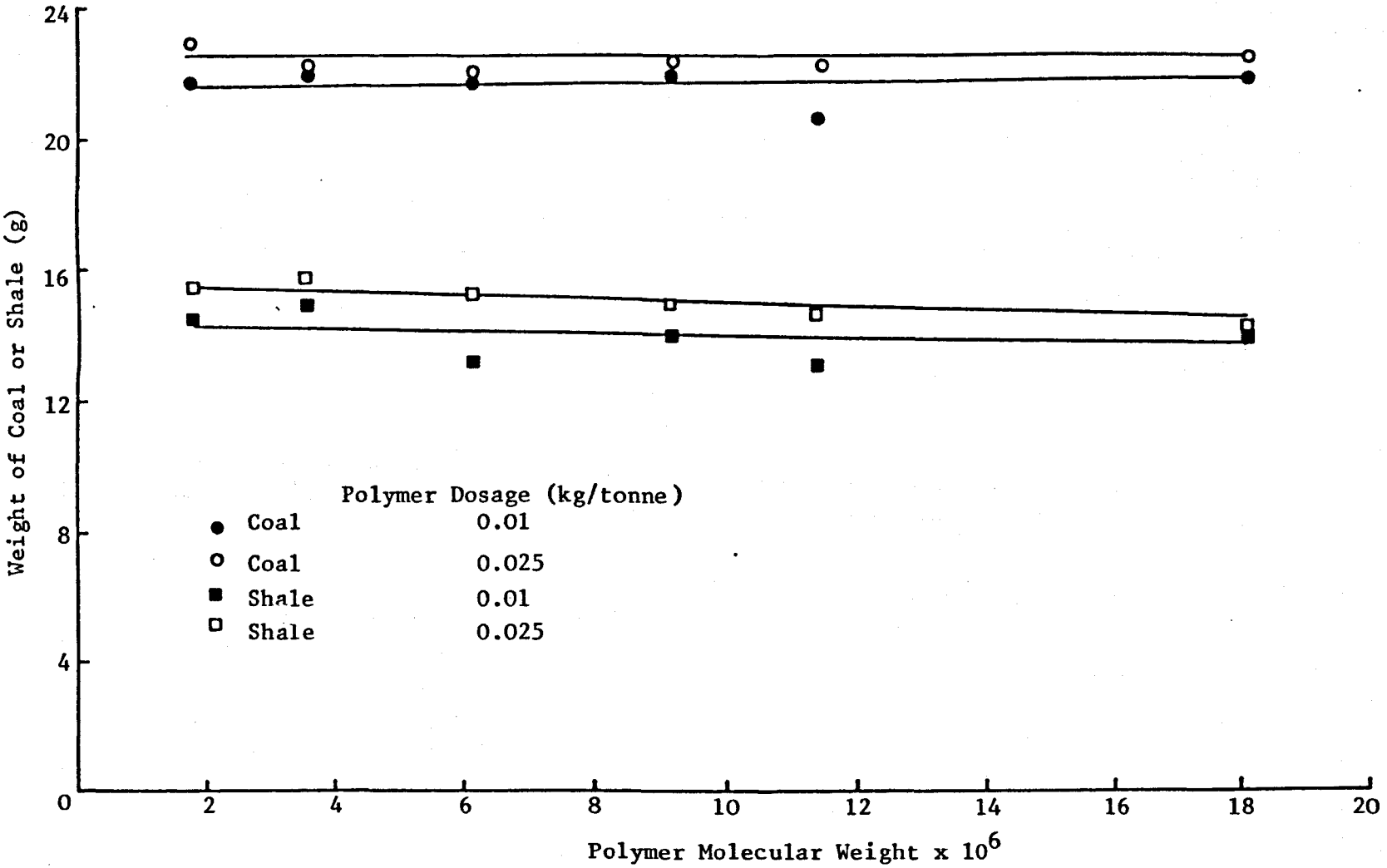


Figure 5.7 Sediment Coal and Shale Weights at High Dispersant Dosage - Non-Ionic Polymers

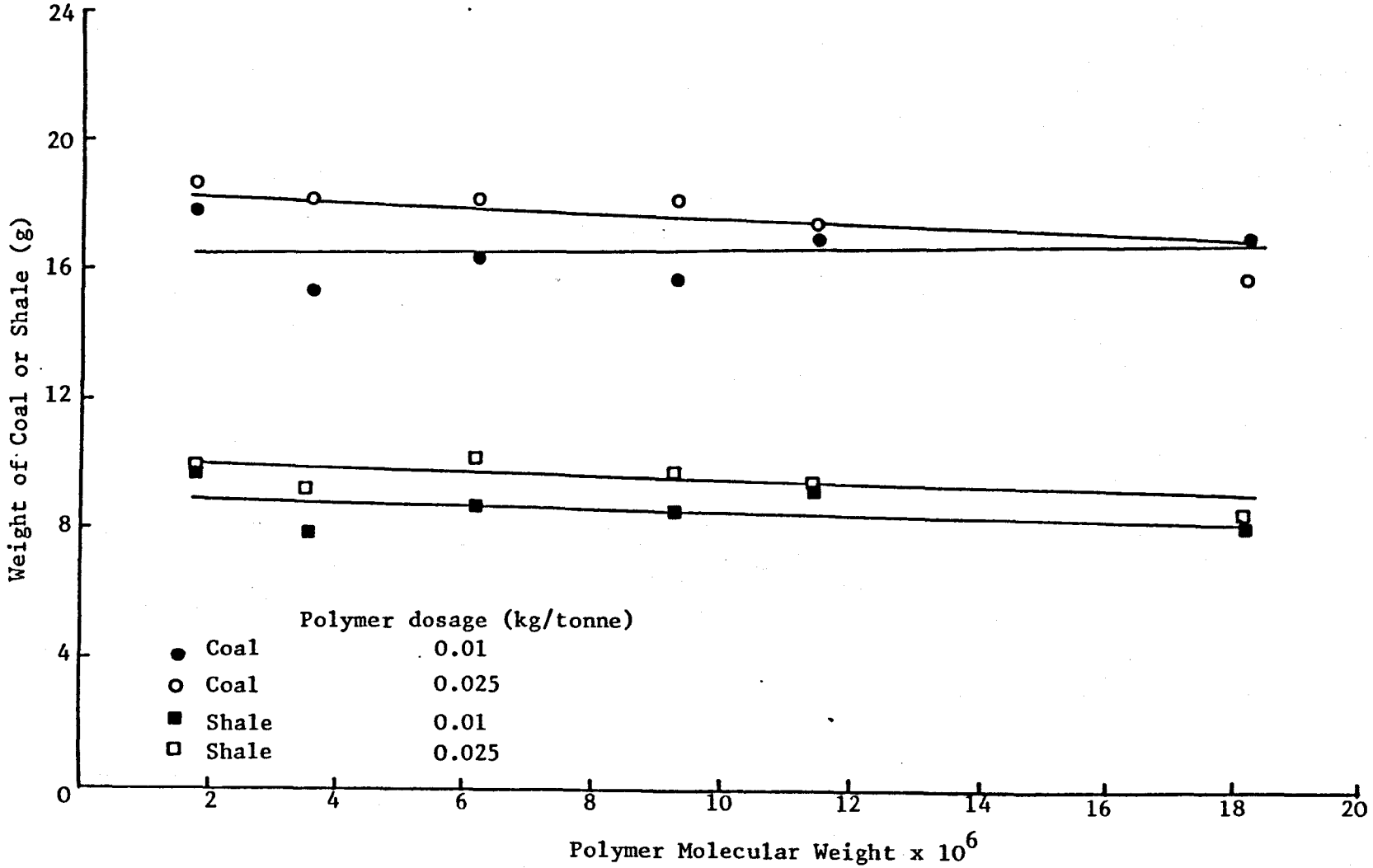


Figure 5.8 Variation of % Sediment Ash - Non-Ionic Polymers

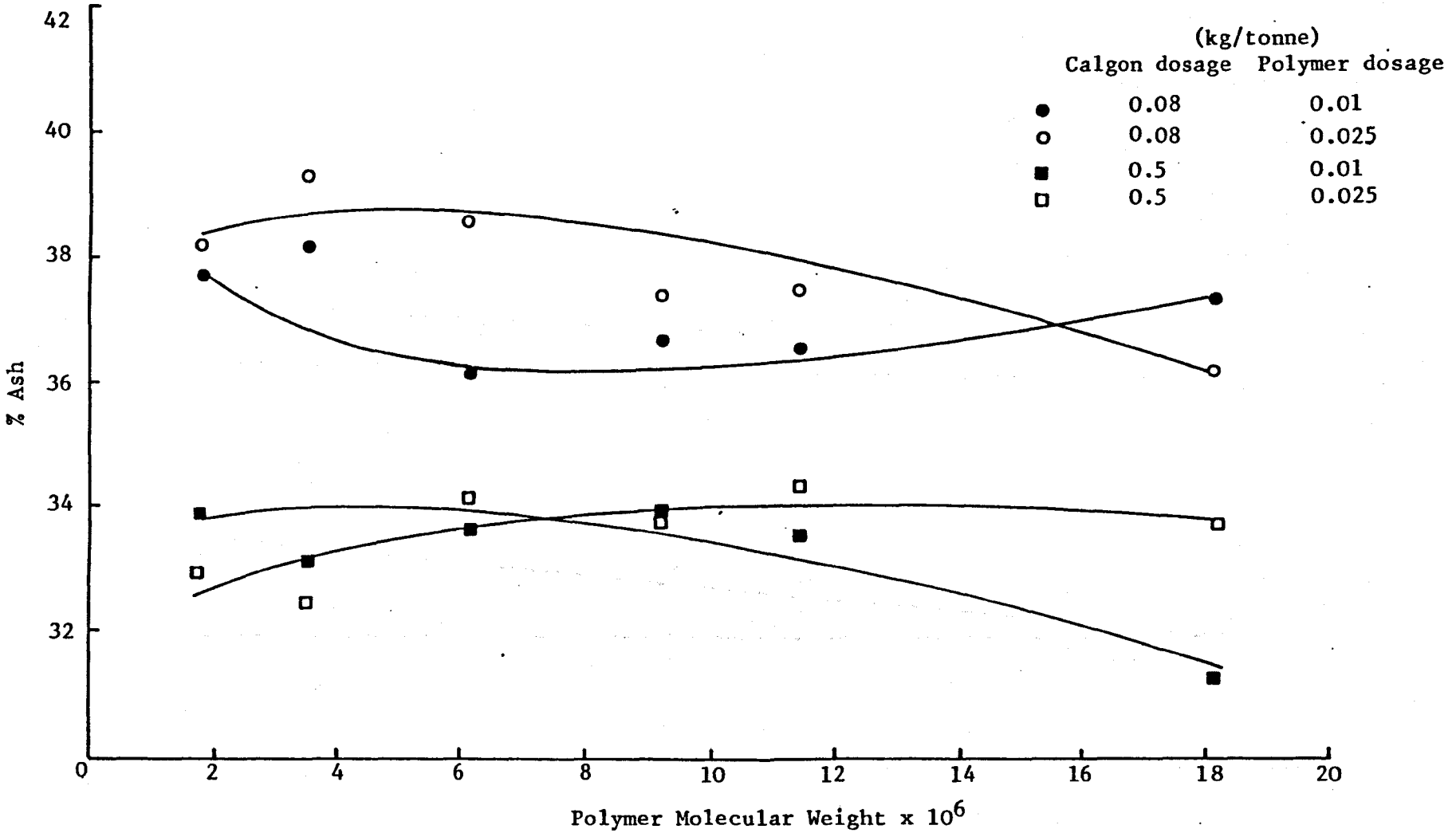


Figure 5.9 Variation of % Weight Yield - Non-Ionic Polymers

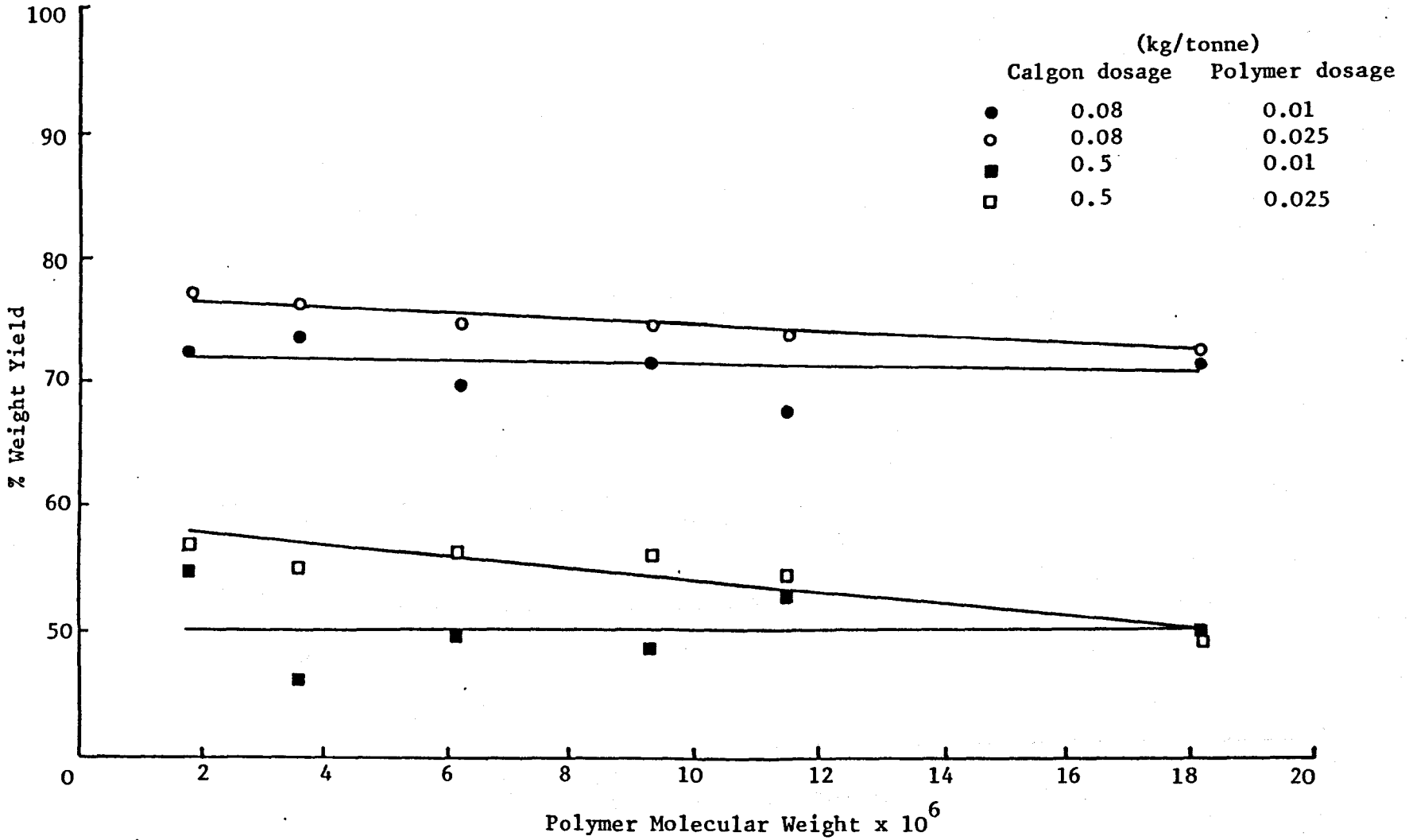
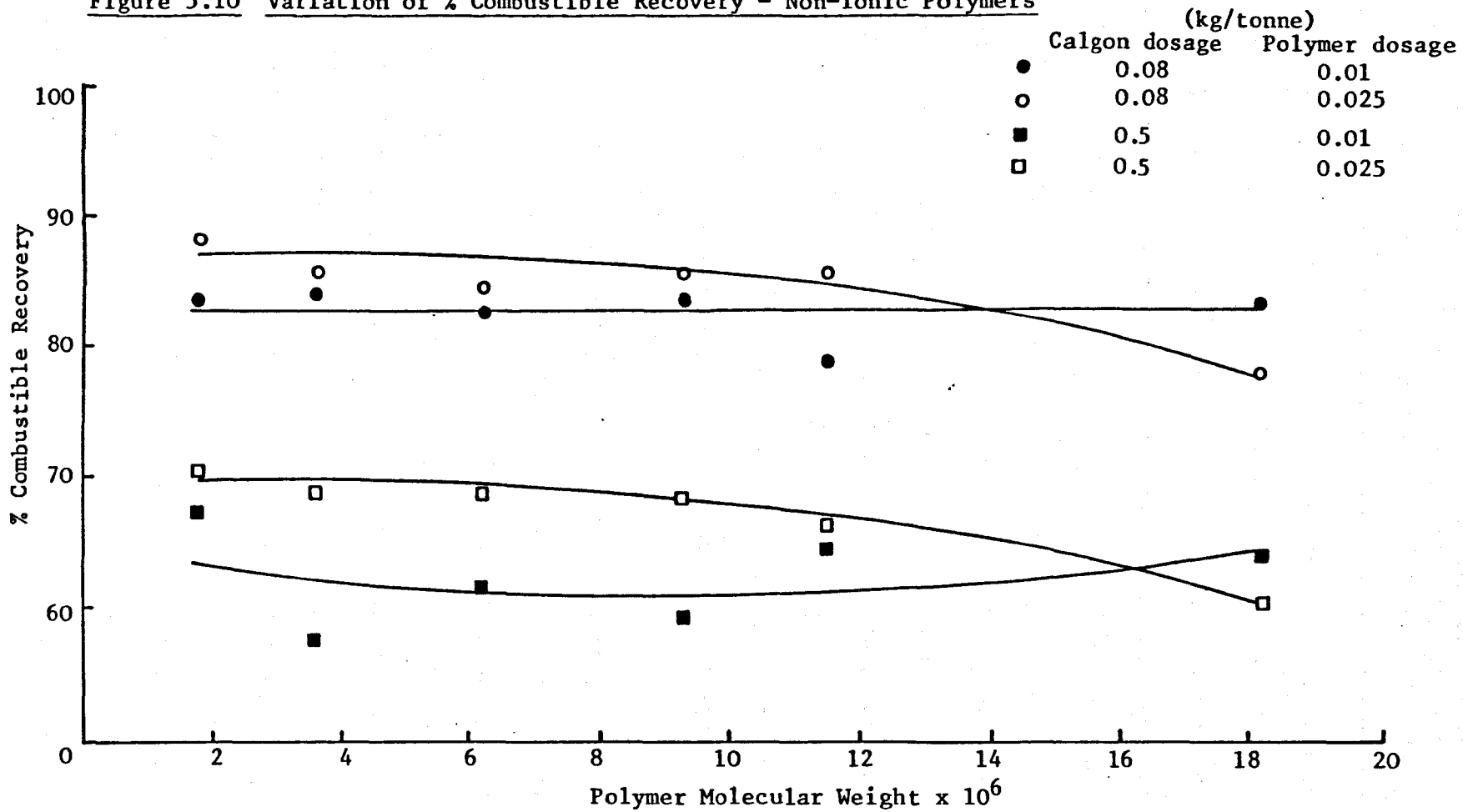


Figure 5.10 Variation of % Combustible Recovery - Non-Ionic Polymers



i(c) The effects of polymer molecular weight are minimal. In the previously conducted settling tests (section 5.1.2(ii) and (iii) using a similar low calgon and low polymer dosage, both coal and shale settling rates had been found to be approximately equal. Thus in a mixed system at low calgon dosage one might anticipate polymer adsorption occurring at both coal and shale surfaces with considerable flocculation of both species; this was apparent. However, at higher calgon dosages although shale settling rates were not influenced significantly, the mass of flocculated solid was affected, as shown by the comparative supernatant clarities (Figure 5.1). On the other hand coal settling rates (and supernatant clarities) were only marginally affected. However, i(a), page 168, suggests that in a mixed system at high calgon dosage flocculation of both species is influenced. From the single specie tests it is difficult to see why the calgon should affect coal flocculation in the mixed system and it is concluded that the additional coal sediment weight produced at low calgon dosage is a result of entrapment by sedimenting shale, rather than by increased flocculation. The reduction in shale sediment weights (at high*** calgon dosages) is however thought to be a direct result of reduced flocculation. Thus an increase in calgon dosage probably increases the zeta potential of the shale (107), but has little or no effect on the coal. This may either inhibit polymer-shale bonding mechanisms or if some adsorption does occur it may not necessarily be followed by bridging, since the extension of the

*** Due to the fact that calgon addition was found to affect the rate of shale flocculation only (section 5.1.2) and presumably therefore only shale surfaces, the effective concentration in a mixed slurry is probably twice that stated; calgon concentration was calculated on the basis of total solids weight, rather than shale weight.

polymer may not be sufficient to offset the tendency of the highly charged shale particles to remain apart. In addition, the effective shale solids concentration is reduced to 2.5% w/v in the selective flocculation tests (as opposed to 5% w/v in the settling tests) and reduces the probability of polymer/surface contact, a condition necessary for effective flocculation. However, regardless of calgon dosage, flocculation of coal is always preferred (for reasons previously discussed in sections 4.2.2 and 4.3.6).

Marginal increases in coal and shale sediment weights suggested in i(b) indicates that the increased availability of polymer resulted in increased flocculation and entrapment of both species.

The results in Tables 5.4 to 5.9 are also described by the trends previously outlined in i(a), i(b) and i(c); i.e. (1) sediment ash contents, weight yields and combustible recoveries are all higher at the low calgon dosage level, (2) the above variables are all increased slightly with an increase in polymer addition, and (3) these variables remain approximately constant despite large variations in polymer molecular weight. No increase in gangue entrainment is apparent with the faster settling flocs, i.e. with the high molecular weight polymers. This is contrary to the suggestions of Yarar and Kitchener (33).

(ii) 50% Anionic Polymers

From an inspection of Tables 5.10 and 5.11 the following points are apparent

Table 5.10 Sediment Coal and Shale Weight at Low Calgon Dosage - 50% Anionic Polymers

Polymer	0.01 kg/tonne polymer		0.025 kg/tonne polymer	
	Wt. of Coal in sediment	Wt. of Shale in sediment	Wt. of Coal in sediment	Wt. of Shale in sediment
G	22.9	17.1	22.4	17.6
H	22.6	14.9	22.2	16.3
I	23.0	16.6	21.2	16.0
J	21.8	15.5	20.4	15.7
K	22.7	16.5	22.4	17.6
L	22.2	15.8	23.2	17.8

Table 5.11 Sediment Coal and Shale Weights at High Calgon Dosage - 50% Anionic Polymers

Polymer	0.01 kg/tonne polymer		0.025 kg/tonne polymer	
	Wt. of Coal in sediment	Wt. of Shale in sediment	Wt. of Coal in sediment	Wt. of Shale in sediment
G	17.4	9.5	17.1	9.0
H	14.8	8.8	20.1	9.7
I	16.3	9.5	15.6	8.3
J	13.8	8.4	13.7	8.5
K	17.6	8.9	17.4	9.3
L	19.7	10.9	19.6	10.9

Table 5.12 Sediment % Ash at Low Dispersant Dosage - 50% Anionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
G	40.1	41.1
H	37.4	39.7
I	39.4	40.3
J	39.1	40.6
K	39.5	41.1
L	39.0	40.5

Table 5.13 Sediment % Ash at High Dispersant Dosage - 50% Anionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
G	33.9	33.2
H	35.4	31.6
I	35.2	33.3
J	35.9	36.4
K	32.5	33.5
L	34.0	34.2

Table 5.14 Weight Yields at Low Dispersant Dosage - 50% Anionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
G	80.0	80.0
H	75.0	77.0
I	79.2	74.4
J	74.6	72.2
K	78.4	79.6
L	76.0	82.0

Table 5.15 Weight Yields at High Dispersant Dosage - 50% Anionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
G	53.8	52.2
H	47.2	59.6
I	51.6	47.8
J	44.4	44.4
K	53.0	53.4
L	61.2	61.0

Table 5.16 Combustible Recoveries at Low Dispersant Dosage - 50% Anionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
G	88.7	87.3
H	86.5	86.0
I	88.9	82.3
J	82.8	86.5
K	87.8	86.8
L	85.9	90.4

Table 5.17 Combustible Recoveries at High Dispersant Dosage - 50% Anionic Polymers

Polymer	Polymer Dosage (kg/tonne)	
	0.01	0.025
G	65.9	64.6
H	58.9	75.5
I	61.9	59.0
J	52.7	52.3
K	66.3	65.8
L	64.8	74.3

Figure 5.11 Sediment Coal and Shale Weights at Low Dispersant Dosage - 50% Anionic Polymers

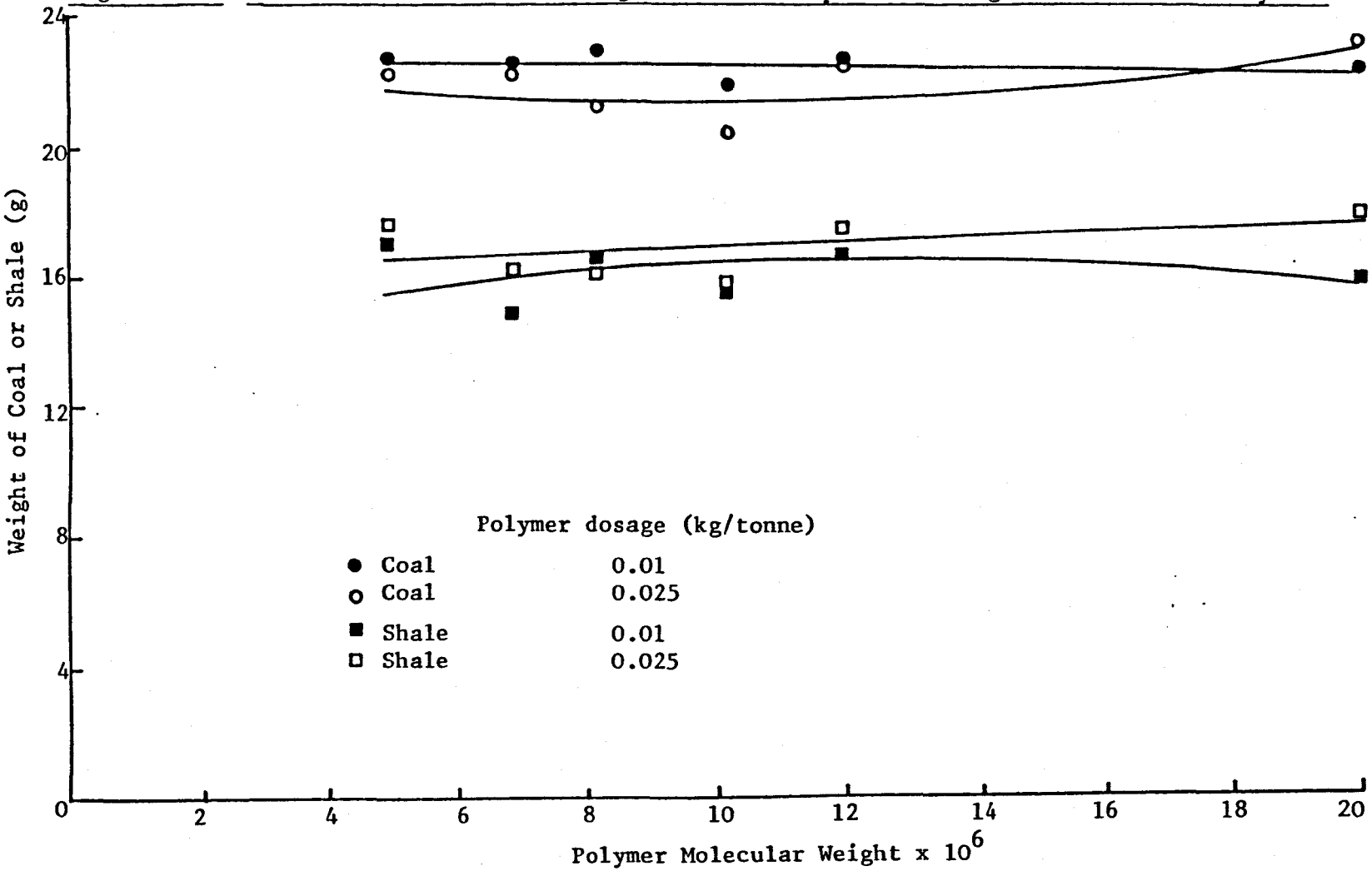


Figure 5.12 Sediment Coal and Shale Weights at High Dispersant Dosage - 50% Anionic Polymers

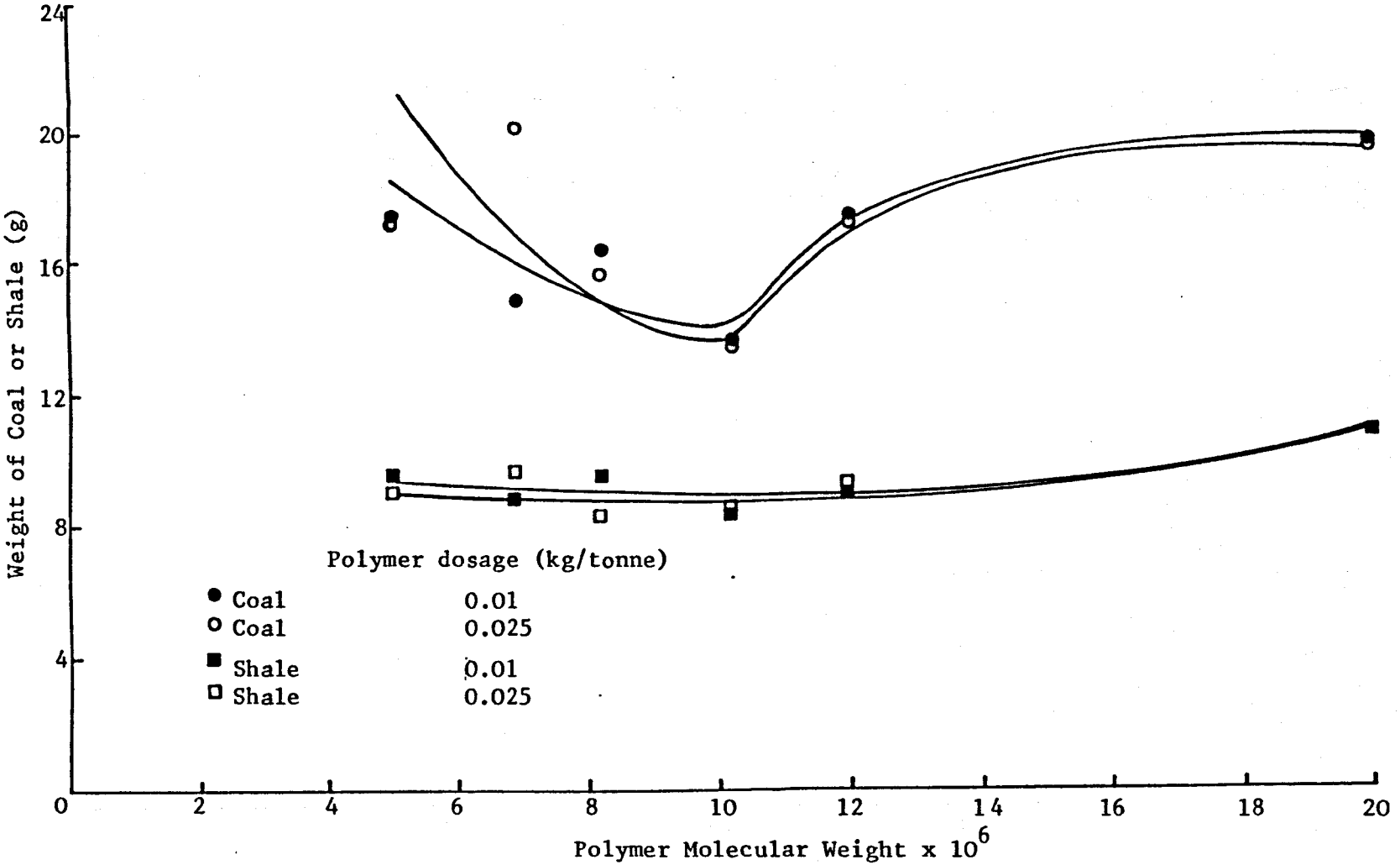


Figure 5.13 Variation of % Sediment Ash - 50% Anionic Polymers

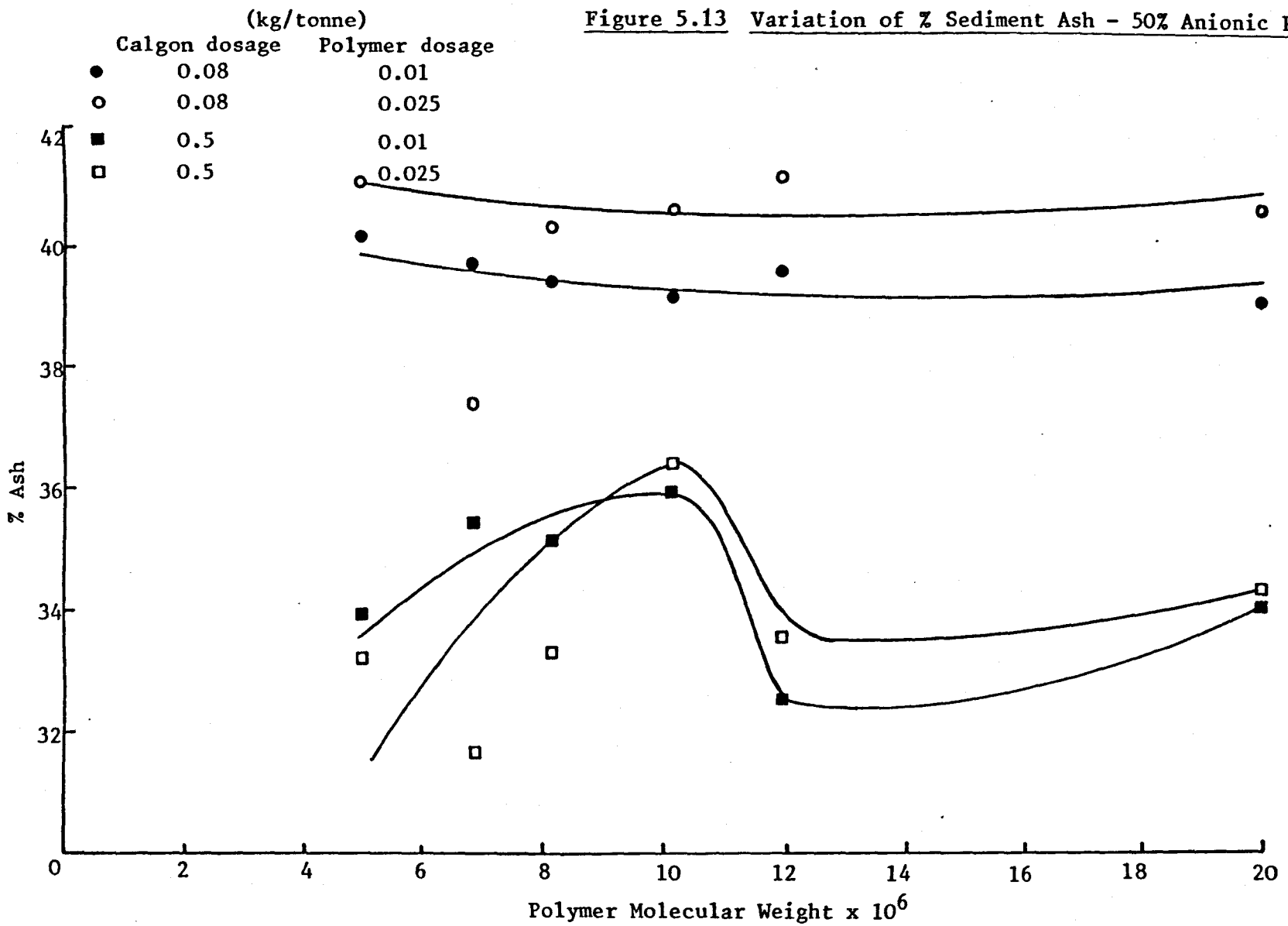


Figure 5.14 Variation of % Weight Yield - 50% Anionic Polymers

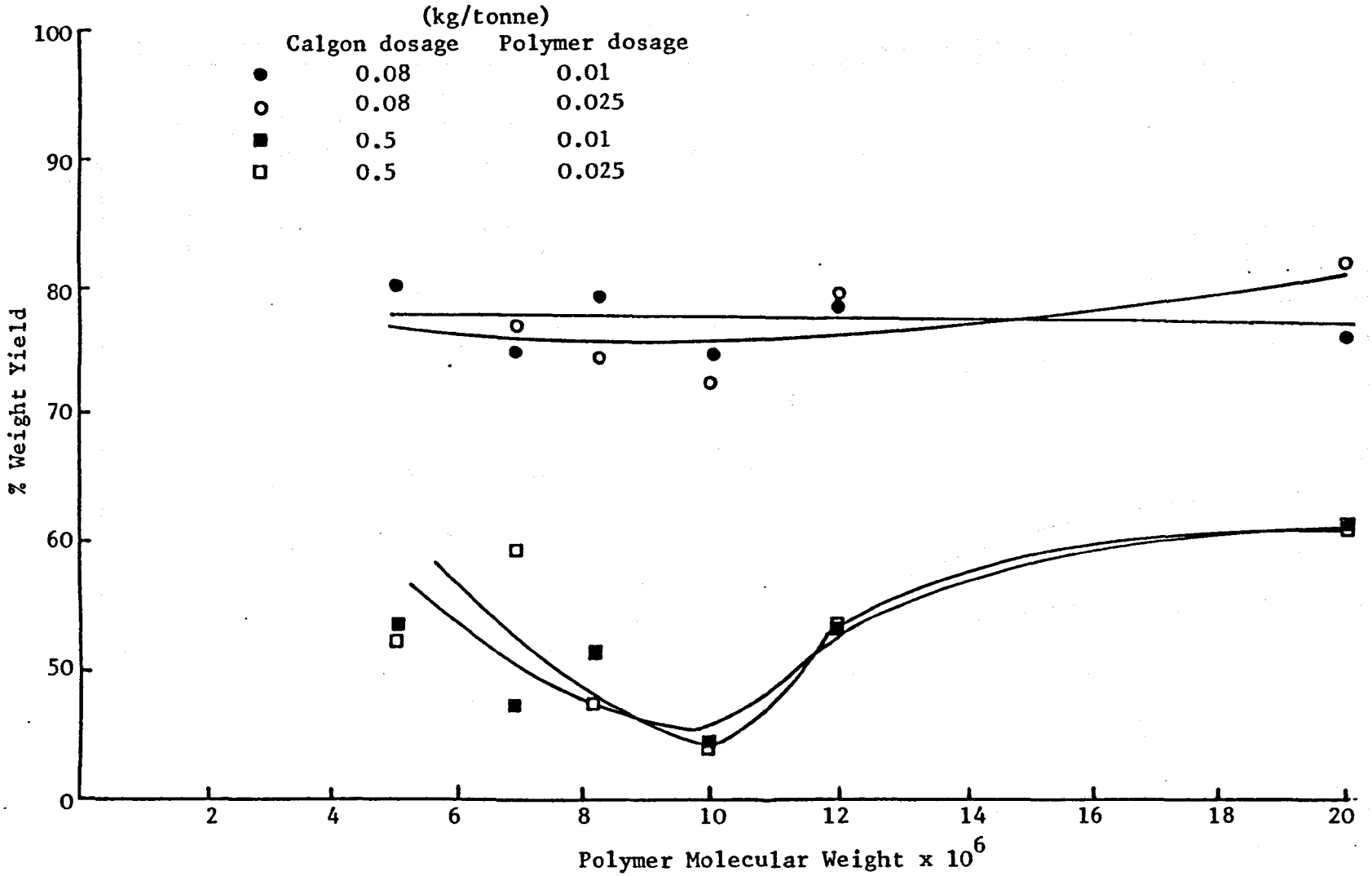
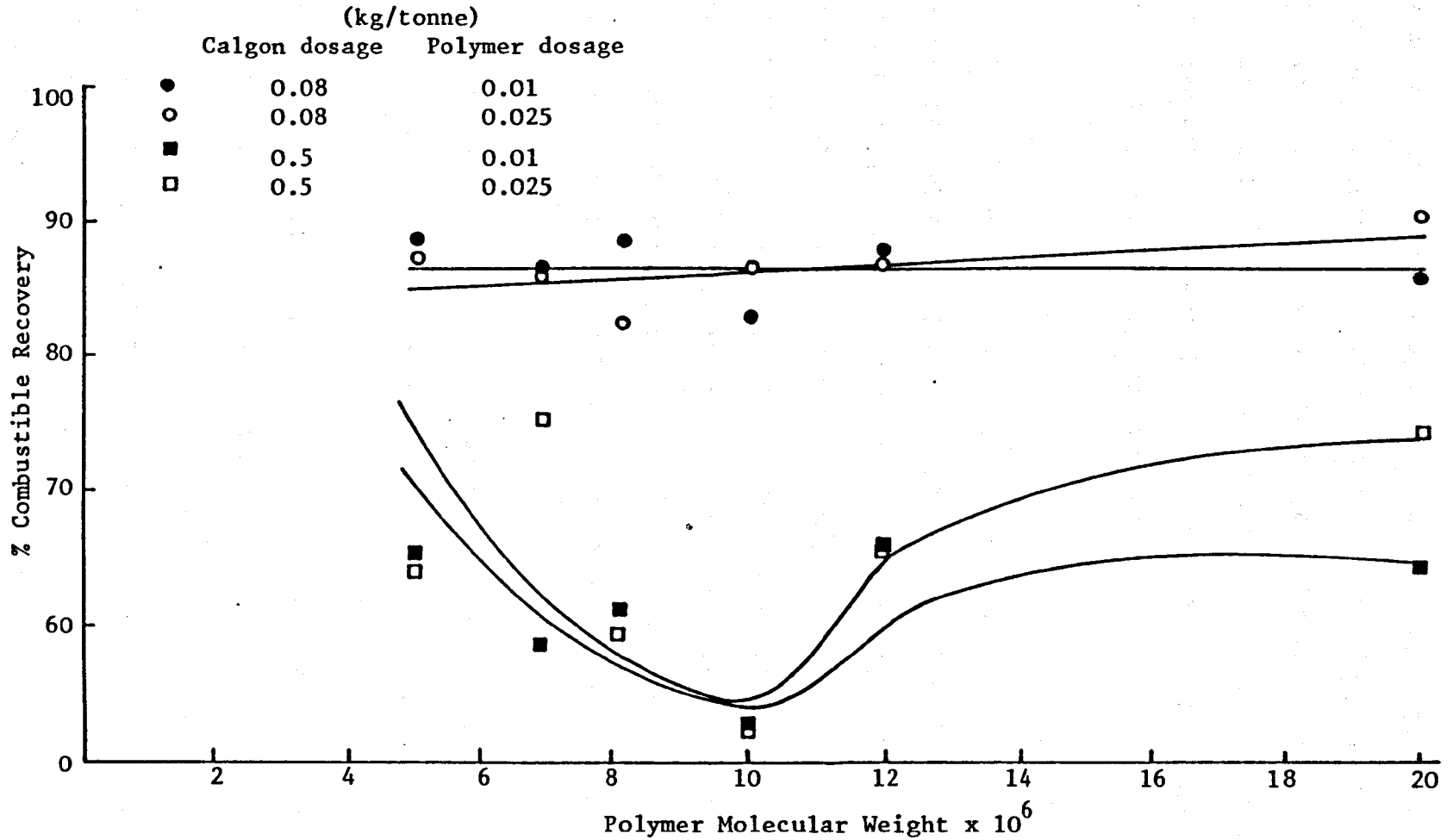


Figure 5.15 Variation of % Combustible Recovery - 50% Anionic Polymers



ii(a) As with the non-ionic polymers, the main effect, is that of dispersant dosage, with higher calgon levels resulting in seemingly increased dispersion of both coal and shale species. Coal/shale ratios are approximately 3:2 at low calgon dosage and 2:1 at the higher dispersant level.

ii(b) Neither coal nor shale sediment weights are affected by increased polymer concentration; this applies at both levels of calgon addition.

ii(c) The effects of polymer molecular weight are minimal, although polymer J possibly indicates some reduced flocculating effects.

From the settling tests described earlier it was apparent that calgon had a minimal effect on coal flocculation but significantly affected shale flocculation (5.1.2(iv) and (v)). Hence as suggested in section (i) of this discussion the additional coal sediment weight at low calgon dosage is due to the entrapment effect, while lower shale sediment weights at high calgon dosage are the result of reduced flocculation. At low calgon dosage near maximum flocculation of coal has been achieved, the suspended material being shale only.

With regard to polymer J, it is suggested that the reduced effects may be a result of some differences in its molecular weight distribution and that more optimum results may be more readily achieved with the remaining five polymers. Healy (26) suggested that the requirements of flocculation are that extended segments are available, that they are of sufficient length and number and that free surface is available for bridge sites. As the polymer

molecular weight is increased β, the number of adsorbed segments per molecule increases, τ, the total number of segments per molecule also increases and $(\tau-\beta)$ the number of extended segments increases slightly. These parameters may not be at an optimum with polymer J. With lower molecular weight polymers β and τ may be reduced but the number of free solid surface sites is high. On the other hand, with higher molecular weight polymers, although more surface may be covered by the polymer the number of extended segments may be increased sufficiently for bridging to occur effectively. The settling tests had also indicated that, at low dosage, polymer J produced reduced coal settling velocities when compared with those of polymers I and K, i.e. polymers having molecular weights immediately below and above J. This was apparent at both calgon levels. Similarly shale settling velocities were reduced for this polymer at the lower calgon dosage. This lends support to the above suggestion that polymer J possesses reduced flocculating ability.

Although exhibiting more variation than the non-ionics Tables 5.12 to 5.17 indicate that with the anionics there is no apparent effect of molecular weight or polymer dosage, except, as stated above, with the possible exception of polymer J. Any fluctuations in ash contents may be a reflection of the pH of the system; it has already been established that a small variation in pH may exert a considerable influence on sediment ash (section 4.4) and hence inconsistencies may be due to some slight variation in pH, or indeed to difficulties in the separation process. In addition it is not really possible to explain variations of $\pm 1.5\%$ in ash content, since reliable determinations are difficult; this problem is also common to flotation testwork.

5.2.3 Summary

It is apparent that an essential prerequisite for selective coal flocculation is to ensure effective shale dispersion; this was evidently not achieved using a calgon dosage of 0.08 kg/tonne. This lends support to suggestions in section 4.2.2 and 4.3.6 that the use of a low calgon dosage in the initial settling tests lead to erroneous predictions regarding selective flocculation, when an increased dosage had been employed, i.e. shale was not selectively flocculated by anionic polymers. It is considered that shale flocculation would have been increased considerably (as indicated by the results of these tests) if the original selective flocculation tests had been conducted at a low calgon dosage. However preferential flocculation of coal would have still resulted. In these tests, on increasing the dosage to 0.5 kg/tonne (effectively 1 kg/tonne) the adsorption of polymer onto shale surfaces was inhibited as a result of increased polymer/surface repulsion. Alternatively, due to insufficient polymer extension it was not followed by bridging; the extent of shale flocculation was consequently decreased. This reduced sediment ash contents by up to 6 percentage points; however levels below 31% were not attainable for these systems. This was the result of both shale entrainment and inevitably some shale flocculation. Removal of the entrained shale was not possible due to the very weak nature of the flocs, which even gentle agitation, ruptured, and would not reform. This is in contrast to the work of Yarar and Kitchener (33) on calcite, quartz and galena systems when gentle agitation or a redispersion-reflocculation stage was successful in reducing the severity of entrapment.

It may therefore be concluded that for the coal/shale slurry under investigation, given sufficient shale dispersion both non-ionic and 50% anionic polymers of various molecular weights will affect reasonable selective coal flocculation at low polymer dosage levels. Under such conditions, products of between 31% - 36% ash with corresponding weight yields of 50% - 60% are possible.

In section 4.6 the possible use of a preconditioner for coal had been investigated. Since this approach had achieved some success it was decided to conduct a further study into the effects of promoter addition with the ultimate aim of reducing ash levels further. Six of the non-ionic and 50% anionic polymers were tested and the findings of the study are described in the following section.

5.3 EFFECT OF PRETREATMENT BY OLEIC ACID AND CREOSOTE

Pretreatment of the coal surface, with creosote, diesel oil or oleic acid in section 4.6, had indicated that reductions in product ash content of up to 9 percentage points could be achieved; a cationic polymer had been used in the initial tests. In order to establish the effect of pretreatment when used with other types of polymer it was decided to conduct tests at various promoter dosage levels while maintaining a constant polymer (0.025 kg/tonne) and dispersant (0.5 kg/tonne) dosage throughout. A polymer dosage level of 0.025 kg/tonne was chosen since in the previous section dosages of 0.01 and 0.025 kg/tonne had produced similar results. Three non-ionic and three anionic polymers were chosen from the twelve available and oleic acid and creosote selected as conditioning reagents.

5.3.1 Experimental

The procedure adopted was similar to that described in section 5.2.1 except that the promoter was introduced prior to dispersion at levels of 0.5, 1.0, 2.0, 4.0 or 5.0 kg/tonne. A series of tests were also conducted at the various dosage levels of oleic acid but omitting polymer addition. Both sediment and supernatant were dried, weighed and ashed in duplicate. Weight yields, combustible recoveries and sediment coal and shale weights were determined as before. The results of all of the tests conducted are tabulated in Appendix 8 and presented graphically in Figures 5.16 to 5.23.

5.3.2 Observations and Discussion of Results

Although sediment coal and shale weights were calculated from a combination of sediment ash content and weight yield, it is considered that, in this instance, they present a clearer representation of both the selectivity and efficiency of the separation process.

(i) Figures 5.16 and 5.17 - Non-Ionics plus Oleic Acid

From Figure 5.16 several observations may be made, these are:

i(a) Coal sediment weights are always higher than those of shale; this gives rise to a product with an ash content considerably lower than 46% (as seen in Figure 5.17).

i(b) With the exception of one point (at 5 kg/tonne oleic acid alone), regardless of polymer type, shale weights are unaffected by oleic acid.

i(c) Between 0.5 and 2 kg/tonne oleic acid the test without polymer addition gave the highest coal recovery.

Figure 5.16 Sediment Coal and Shale Weights at Various Oleic Acid Dosage Levels - Non-Ionic Polymers

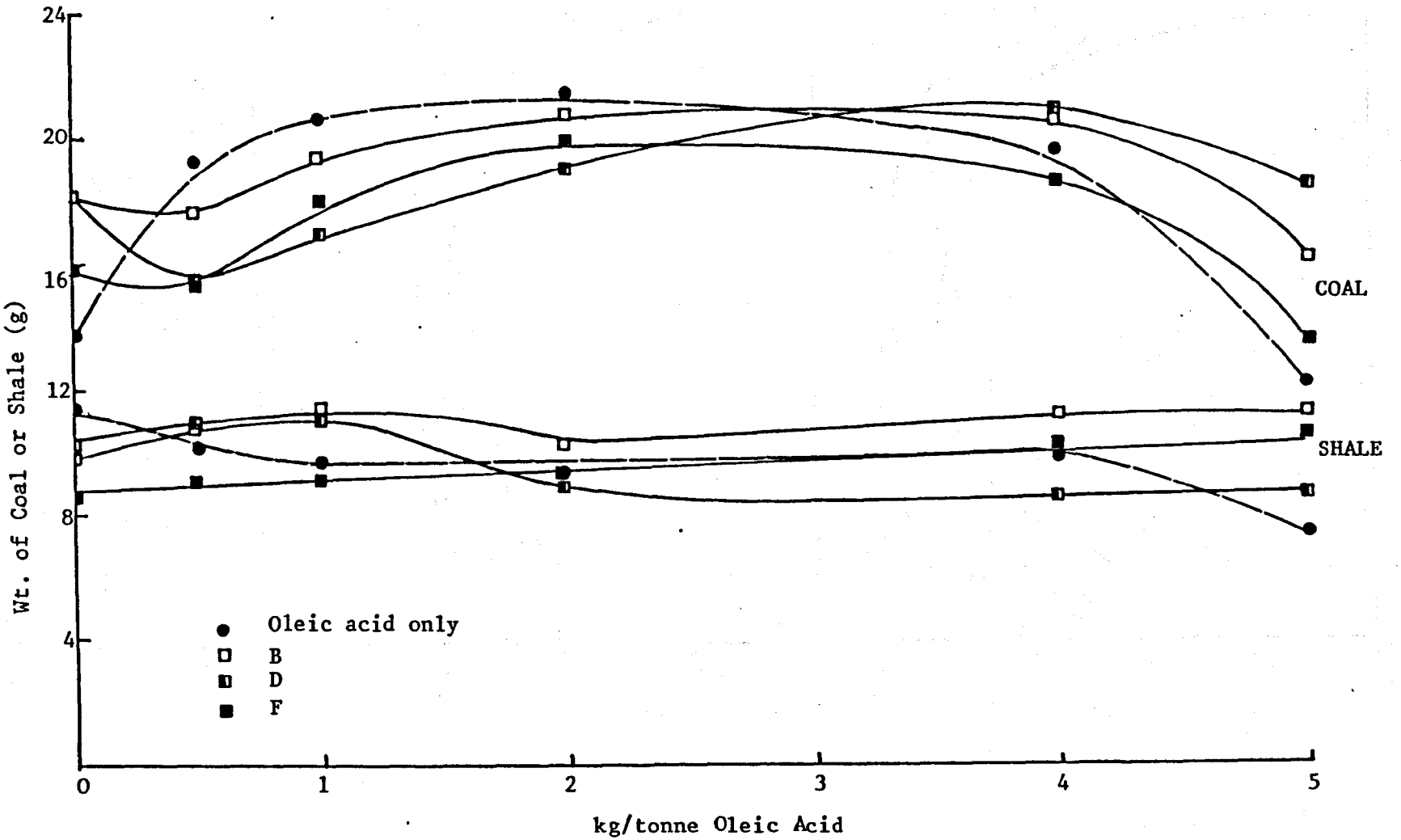
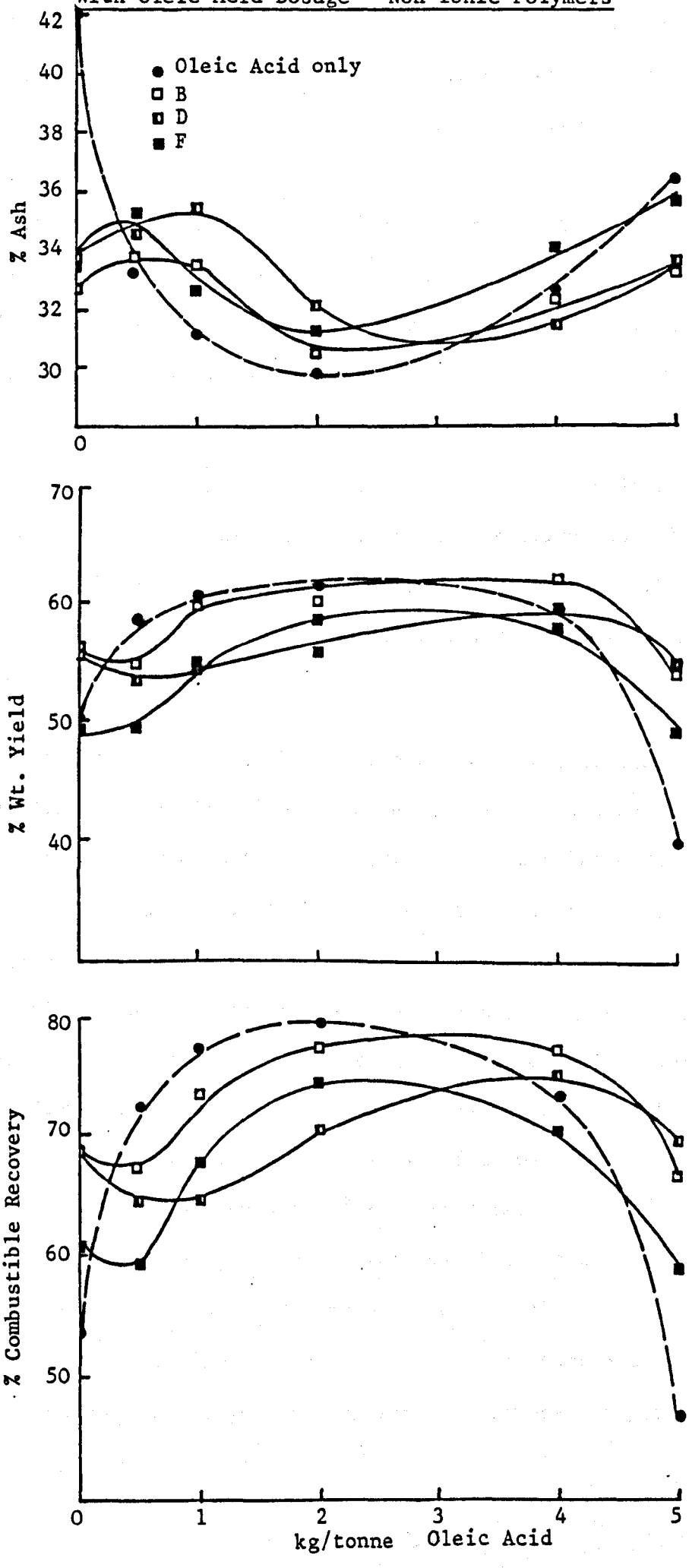


Figure 5.17 Variation of % Ash, Wt. Yield and Combustible Recovery With Oleic Acid Dosage - Non-Ionic Polymers



i(d) Below 2 kg/tonne, coal sediment weights for the tests using oleic acid alone generally increased with increasing dosage of oleic acid. The oleic acid plus polymer curves follow similar, but reduced, trends.

i(e) Above 4 kg/tonne the coal sediment weight for the test using oleic acid alone was reduced significantly.

i(f) For the remaining tests, with polymer addition, all polymers gave a similar, but reduced effect from that described in i(e).

Point i(b) concerns the lack of shale response to increasing dosages of oleic acid; this was also shown in section 4.6. In the presence of calgon the shale surface will be negative and the effects of the oleic acid appear minimal i.e. dispersion is not improved.

Point i(c) relates to the agglomerating effect of oleic acid. This was discussed earlier in section 4.6, where it was suggested that it was a result of a form of "hydrophobic coagulation". Also from i(c) it is apparent that the subsequent addition of a polymer to an oleic acid treated coal surface is detrimental to coal agglomeration. This applies to the use of oleic acid as a selective agglomeration reagent and does not relate to the overall separation process; Figure 5.16 indicates that oleic acid is beneficial to the latter system. The flocculation which follows pretreatment by oleic acid will depend upon several factors namely:

(1) the degree of surface coverage by oleic acid

(2) possible modes of adsorption of oleic acid

(3) the orientation with which particles contact each other and

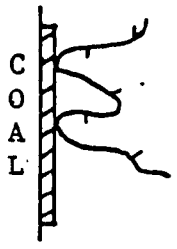
(4) the type of polymer adsorption at the untreated/treated coal surface.

It has been suggested (118a) that the relation between the adsorbing mineral and a fatty acid, such as oleic acid, is not one of simple monolayer formation and as such may indicate a patchwork effect. Possible modes of adsorption of oleic acid were previously suggested in section 4.6 as either polar attachment, facilitated by calcium ions, or physical adsorption at non-polar coal surface sites. The absence of any effect on shale (as shown in Figure 5.16) however suggests that physical adsorption is more probable. On the other hand, if reverse adsorption were to occur it would be more probable at the coal surface due to the added attraction of the non-polar chains already adsorbed. The last two points ((3) and (4) above) are illustrated in Figure 5.24 over.

In order to explain the reduction in coal sediment weight with the addition of polymer, the situation described by Figure 5.24(a) is undoubtedly present. These reductions however are marginal and the mechanisms described by Figure 5.24(b), (c) and (d) must predominate. The whole system is a balance between the effects shown in Figure 5.24, and in order to explain the lower portions of the curves (point i(d)) shown in Figure 5.16 both "hydrophobic coagulation" and polymer flocculation must be considered. For the oleic acid only system the situation illustrated by Figure 5.24(d) must apply, with increasing dosages of oleic acid resulting in increased coal sediment weights. As oleic acid is added prior to flocculant addition, it is probable that much of the system described by the oleic acid curve will again be present. Therefore on the addition of a polymer, some coal will have agglomerated and sedimented out of the system. For the remainder, the situations described in Figures 5.24(a) to (c) will apply.

Figure 5.24 Mechanisms of "Flocculation" following Coal Pretreatment with Oleic Acid

(a)

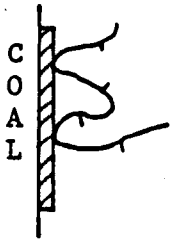


(i)

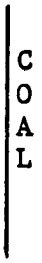
(ii)

Polymer hydrophobically attached to oleic acid treated coal surface (i). H-bonding (or electrostatic bridge formation) unlikely with surface (ii) although some hydrophobic interactions may result; the net effect however is an apparent reduction in flocculation.

(b)



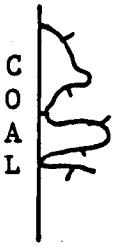
(iii)



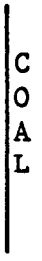
(iv)

Polymer hydrophobically attached to oleic acid treated coal surface (iii). H-bonding (electrostatic bridge formation) and hydrophobic interactions all possible with surface (iv)

(c)



(v)



(vi)

Polymer adsorption and bridging occurs normally i.e. neither surface affected by oleic acid addition.

(d)

(vii)

(viii)

No polymer present Agglomeration between the two treated coal surfaces via "hydrophobic coagulation". This situation could occur prior to flocculant addition.

Although the net effect is seemingly one of increased efficiency for the polymer system it is considered that this is in fact a result of slightly impaired efficiency for the oleic acid.

Regarding the reduction in coal and shale sediment weights noted in points i(e) and i(f), the occurrence of froth flotation was observed. It is assumed that this was as a result of air entrainment during the dispersion stage. If coal is floated then invariably it will entrain some shale (118b), after the cessation of mixing, particularly at the low shear rates employed. It is considered that this would account for the reduction in both coal and shale sediment weights in excess of 4 kg/tonne oleic acid. The addition of oleic acid will increase coal hydrophobicity and hence the flotation effect, absent in earlier tests with no promoter, will appear. The final point relating to Figure 5.16 (i(f)) is the seemingly reduced flotation effect in the presence of a polymer. It is recognised that polymer presence in coal flotation is detrimental; this is currently the subject of a research programme at the University of Cardiff (Private Communication, K. Williams, University of Cardiff). As yet this work is at an early stage and although the effects are present, no explanation is available. On a more practical side a proportion of the floated coal may in fact be brought back into suspension by the agitation provided during polymer addition, and possibly flocculated, along with some of the entrained shale; this would decrease the flotation effect.

Thus to summarise, although the effect of pretreatment with oleic acid does not necessarily improve the selectivity of polymer

flocculation, it does improve both the efficiency and selectivity of the overall separation process. This however is more attributable to 'flocculation' by oleic acid than to improved polymer performance.

(ii) Figures 5.18 and 5.19 - 50% Anionics Plus Oleic Acid

From Figure 5.18 several points are apparent, these are:

ii(a) Coal sediment weights are always higher than those of shale; this gives rise to a product of below 46% ash content (as illustrated in Figure 5.19).

ii(b) As noted in section (i) of this discussion, the shale sediment weight is marginally reduced at 5 kg/tonne oleic acid alone. It is also reduced at low oleic acid levels, (i.e. 0.5 to 1 kg/tonne) with polymer addition.

ii(c) Between 0.5 to 4 kg/tonne oleic acid the test without polymer addition gave the highest coal recovery.

ii(d) Below 2 kg/tonne oleic acid coal sediment weights for the test using oleic acid alone generally increased with increasing oleic acid dosage.

ii(e) For the oleic acid plus polymer curves reductions in coal sediment weights, when compared with the zero point of addition, are noted at levels up to 1 kg/tonne.

ii(f) At levels of between 1 to 2 kg/tonne oleic acid plus polymer, coal sediment weights are increased.

ii(g) Above 4 kg/tonne the coal sediment weight for the test using oleic acid alone is reduced significantly and two of the tests with polymer addition follow a similar, but reduced, trend. For one point (5 kg/tonne oleic acid plus polymer L) the coal sediment weight is further reduced.

Figure 5.18 Sediment Coal and Shale Weights at Various Oleic Acid Dosage Levels - 50% Anionic Polymers

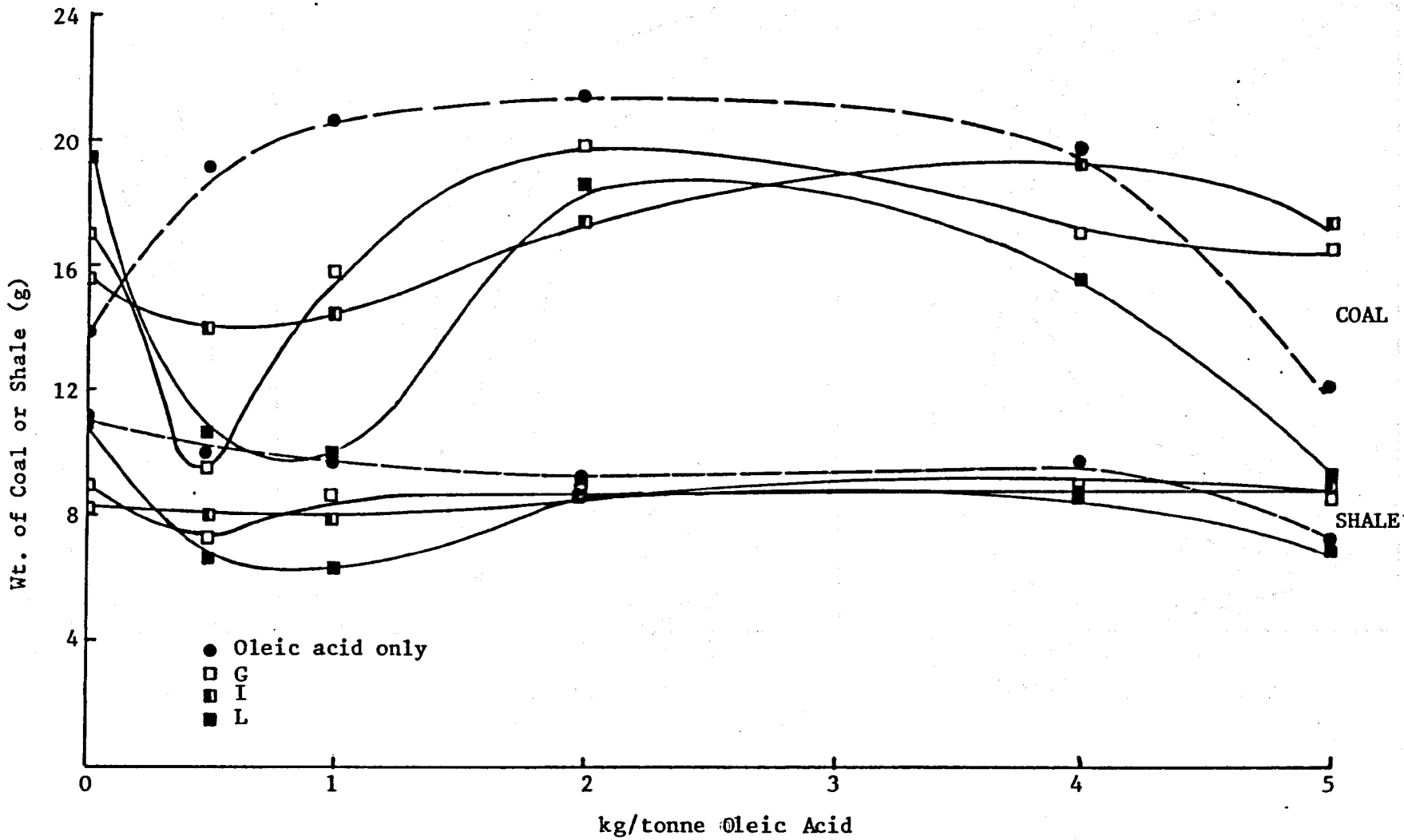
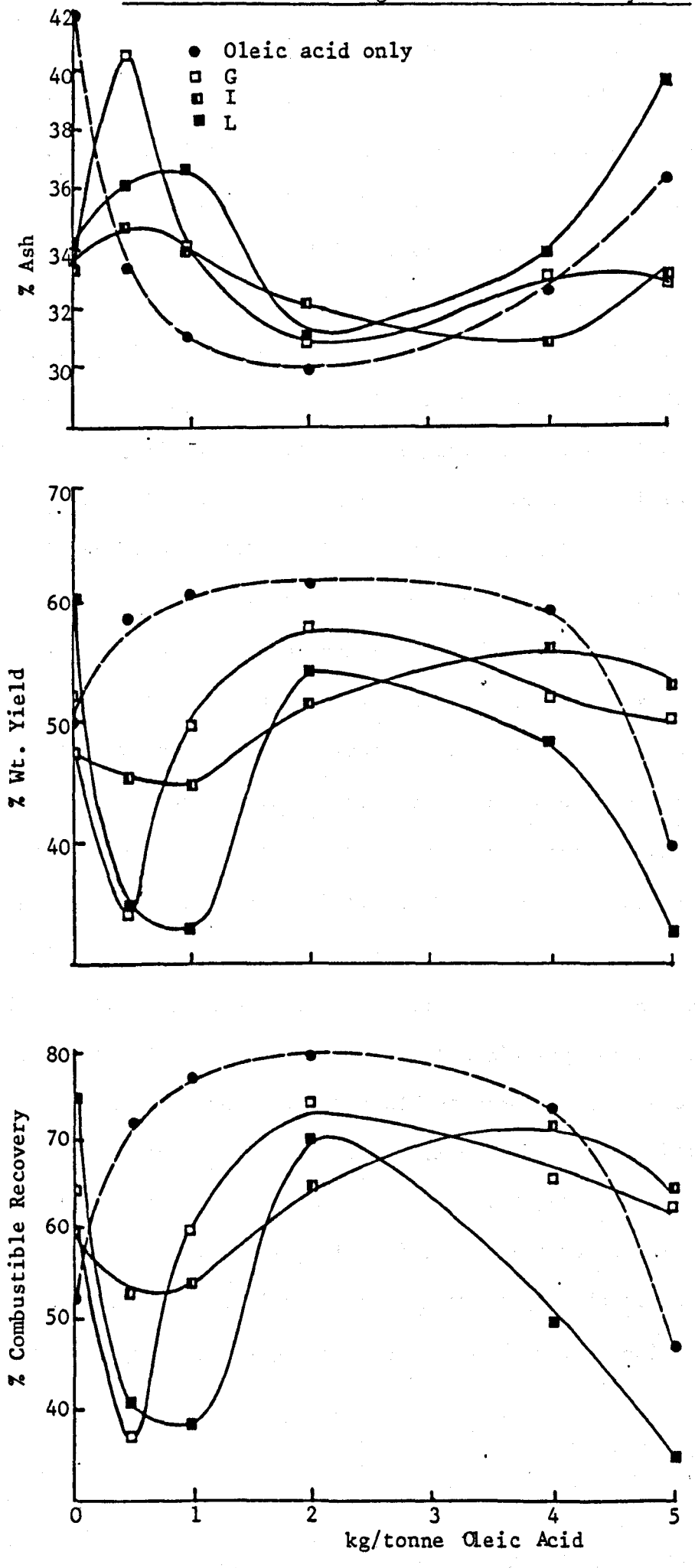


Figure 5.19 Variation of % Ash, Wt. Yield and Combustible Recovery With Oleic Acid Dosage - 50% Anionic Polymers



The suggestions previously outlined in section (i) of this discussion regarding the agglomerating effect of oleic acid addition alone are also applicable here. Similarly the explanation of points i(b), i(e) and i(f), regarding the lack of shale response (at certain dosage levels only) and the flotation effects will also apply here. Also as in section (i), it is apparent that for these systems, the addition of a polymer to the pretreated coal surface is detrimental to the agglomerating effect of the oleic acid, although not necessarily to the overall separation system. However as noted in ii(b), ii(e) and ii(g) the trends are different to those in section (i); this particularly relates to the fall in sediment weights between 0.5 and 1 kg/tonne. Since the only difference between the two systems is the type of polymer employed, the variation in results must be due to the increased polymer anionicity. It is considered that Figure 5.24 will still represent the mechanisms involved in the separation process following polymer addition, but electrostatic bridge formation will now become a far more important bonding mechanism. Since this is initiated through calcium ions in solution, the ability of the polymer to adsorb via this mechanism may have been reduced following some depletion of calcium ions; these may have already facilitated the adsorption of oleic acid via its ionic headgroup. The flocculating ability of the polymers would then be reduced. This effect appears to be most apparent at low oleic acid levels (i.e. 0.5 to 1 kg/tonne) where a lower mass of coal is agglomerated and sedimented prior to flocculant addition i.e. the majority of the coal remains suspended and is hence available for flocculation. The large reductions in coal sediment weights at these low dosage levels is also believed

to account for the much smaller reduction in shale sediment weights i.e. entrainment is less prevalent. Hence once again the whole system is a balance between the effects outlined in Figure 5.24(a), (b), (c) and (d), but with the added complication of anionic adsorption mechanisms.

Point ii(g) suggests that polymer L is less suitable for the flocculation of both floated coal and pretreated coal. Although little effect of molecular weight has previously been observed it appears that in this system the very high polymer molecular weight had a detrimental effect.

To summarise, due to the additional effects of polymer anionicity, under the most favourable conditions, the addition of oleic acid produces only marginal improvements in selectivity and efficiency, and at the worst results in significant reductions in both.

(iii) Figures 5.20 and 5.21 - Non-Ionics Plus Creosote

From Figure 5.20 it may be observed that both coal and shale sediment weights are increased marginally with creosote dosages of up to 1 kg/tonne; above this they tend to level out. It is therefore suggested that the increased hydrophobicity which the creosote undoubtedly imparts to the coal surface improves the selectivity of the flocculation process. However an increase in coal sediment weight is unfortunately accompanied by an increase in entrained shale. Maximum hydrophobicity and hence maximum coal sediment weights are apparent at around 1 kg/tonne; this is also typical of the optimum creosote dosage level applicable in coal

Figure 5.20 Sediment Coal and Shale Weights at Various Creosote Dosage Levels - Non-Ionic Polymers

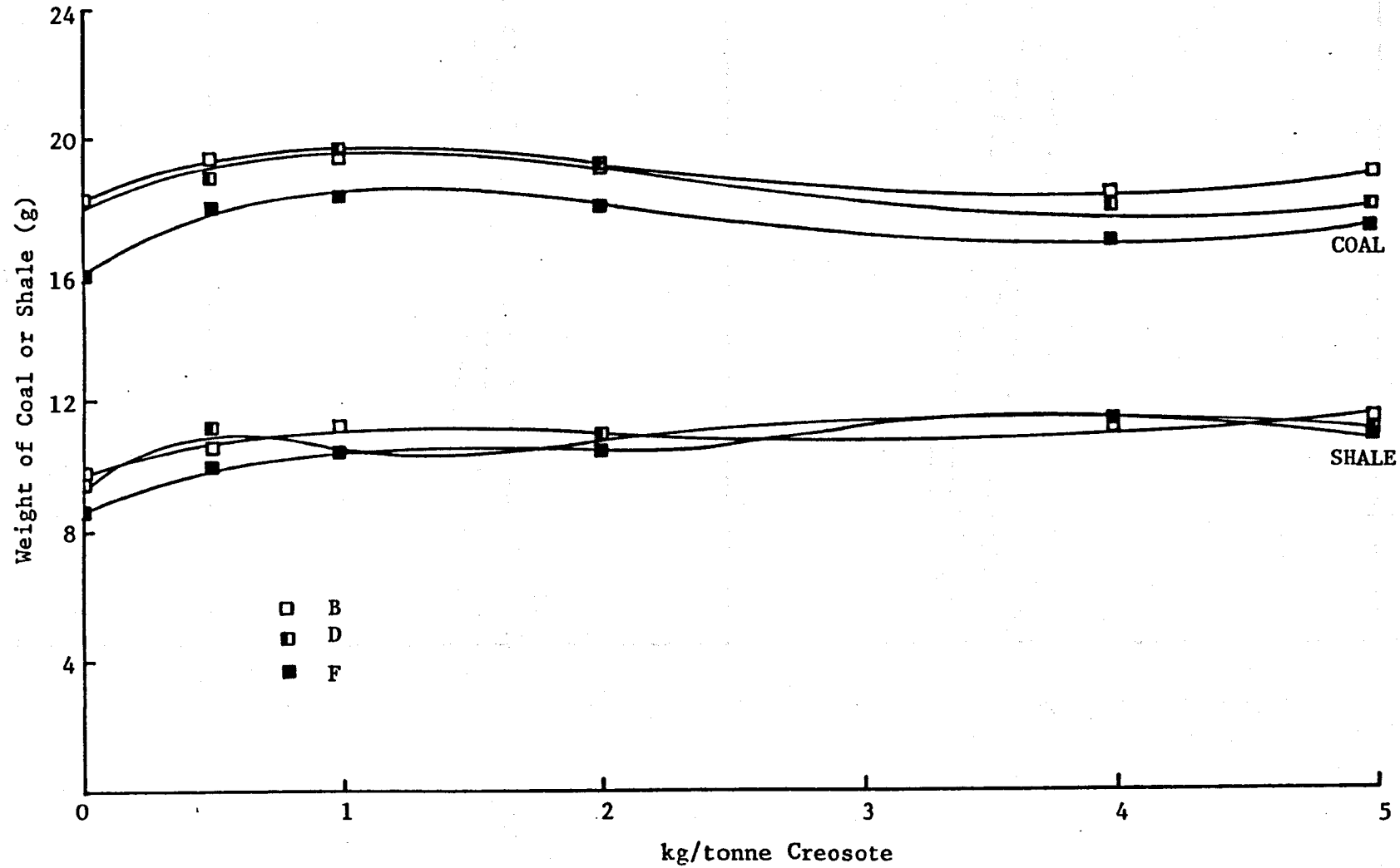
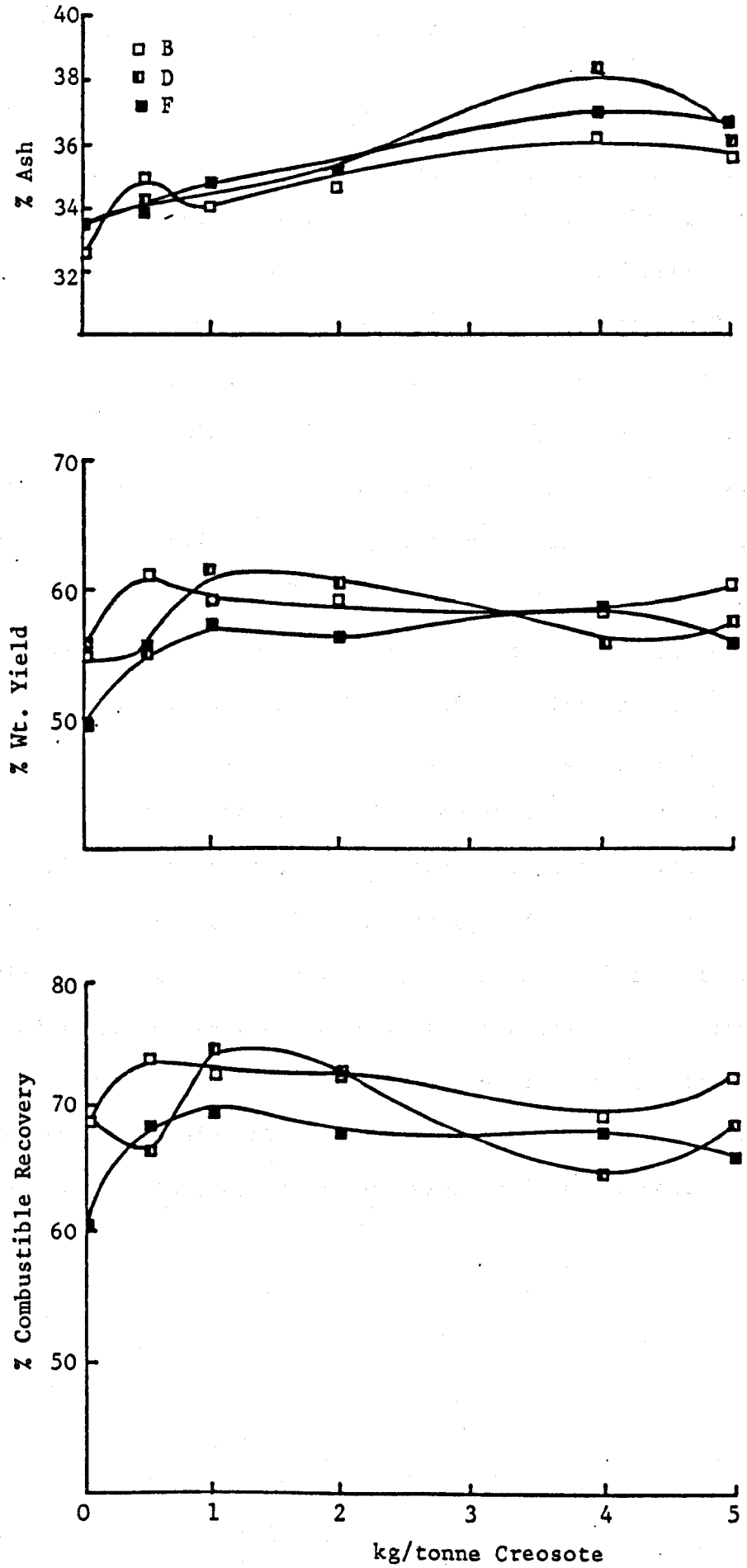


Figure 5.21 Variation of % Ash, Wt. Yield and Combustible Recovery With Creosote Dosage - Non-Ionic Polymers



flotation. Above 1 kg/tonne no further improvements in selectivity are apparent. As illustrated in Figure 5.21, the overall effect of creosote addition on % ash, weight yield and combustible recovery is marginal.

(iv) Figures 5.22 and 5.23 - 50% Anionics Plus Creosote

Up to 2 kg/tonne, apart from small variations, the effect of creosote addition appears to be very similar to that described above. However, maximum flocculation is apparent at around 2 kg/tonne, above which both coal and shale sediment weights are reduced. The increases in shale sediment weights at up to 2 kg/tonne are believed to be directly linked to the increased coal sediment weights also observed at these levels i.e. shale entrainment is enhanced. It is suggested that the reduction in coal sediment weights at creosote dosage levels above 2 kg/tonne may be due to a loss of bonding sites for the anionic polymer. The addition of larger dosages of creosote may mask some of the negative surface sites previously utilised for hydrogen bonding and electrostatic bridge formation. Although additional hydrophobic sites may be available, the net result is apparently a reduction in bonding and hence a decrease in coal sediment weight. Thus to summarise, the overall effect of creosote additions up to 2 kg/tonne is to increase coal sediment weights by improving polymer selectivity, but at the same time increasing shale entrainment. As a result the product ash levels are not significantly reduced at any creosote dosage level.

Figure 5.22 Sediment Coal and Shale Weights at Various Creosote Dosage Levels - 50% Anionic Polymers

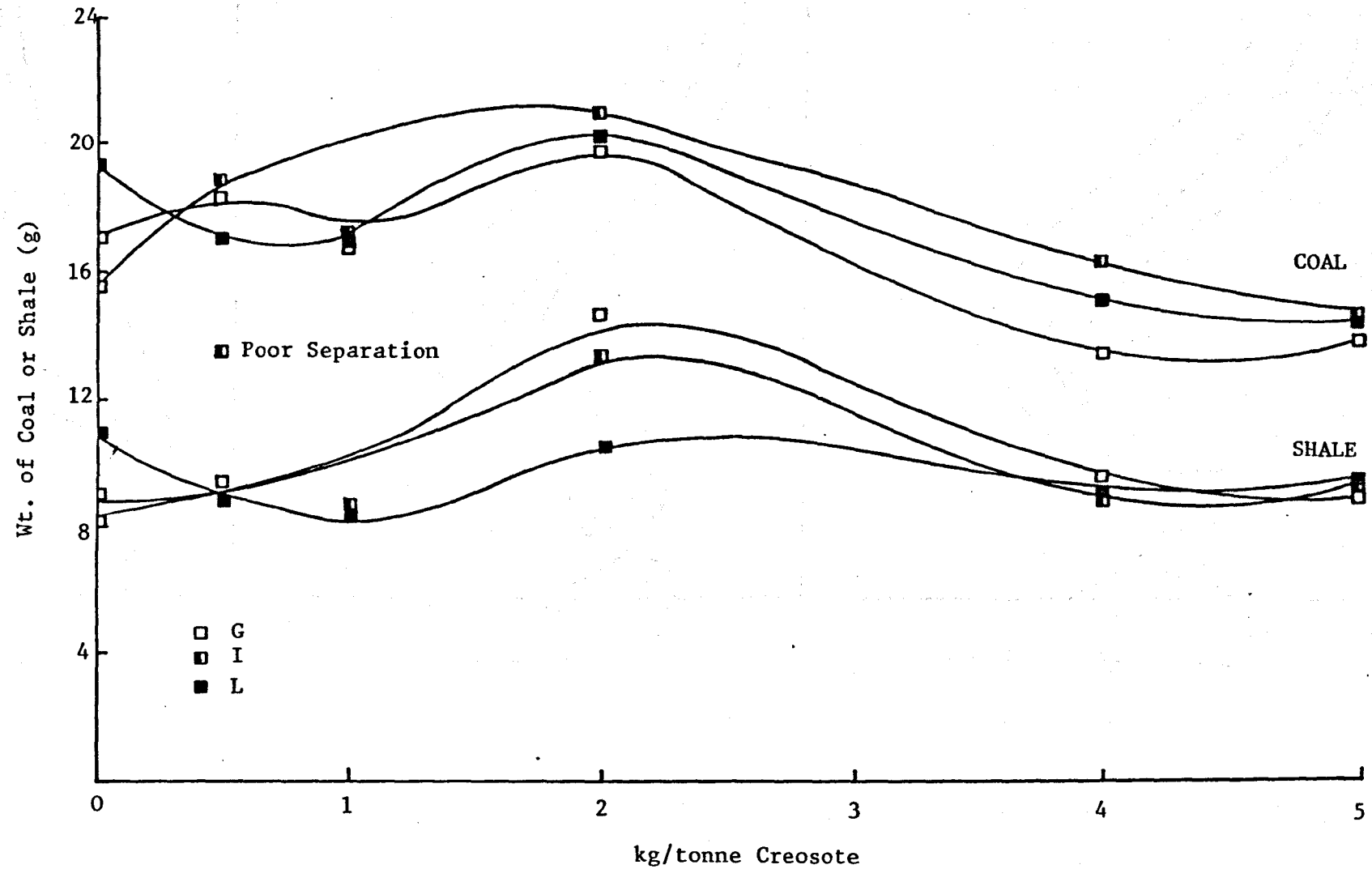
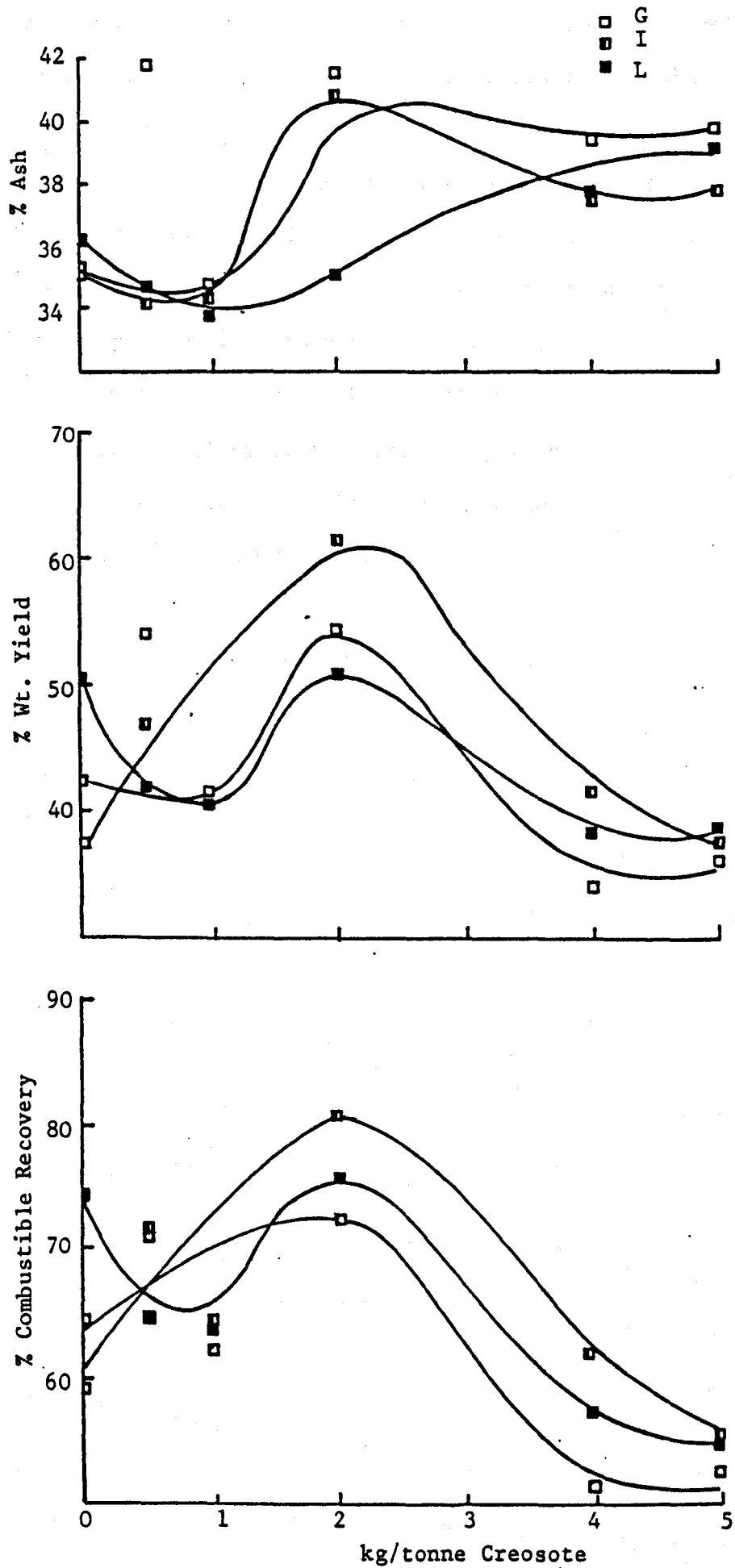


Figure 5.23 Variation of % Ash, Wt. Yield and Combustible Recovery With Creosote Dosage - 50% Anionic Polymers



5.3.3 Summary

While preconditioning of the coal surface prior to flocculant addition may improve hydrophobic polymer interactions and result in marginally increased coal sediment weights, the overall effect, due both to entrained and flocculated shale, is an unacceptably high ash product. This is in addition to some apparent detrimental effects to hydrogen bonding and electrostatic bonding mechanisms, i.e. the inherent hydrophilic nature of the polyacrylamide polymers. It is therefore concluded that, while preconditioning the coal surface prior to flocculant addition may improve selectivity, it is insufficient to achieve an acceptable grade of product; thus the process remains unviable.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 CONCLUSIONS

The conclusions of this work have been discussed and summarised at the end of each section and as such require only restatement.

Settling tests carried out initially on separate pure coal and shale slurries in the presence of calgon (0.08 kg/tonne) indicated that, in general, settling velocities were increased with an increase in polymer dosage. High settling velocities were obtained for shale using anionic polymers. The exception to this was the 100% anionic polymer when excess polymer/surface repulsion lead to a loss of flocculating power. For coal, cationics were more effective while non-ionics produced similar settling velocities for both species. The above was apparent for all polymers of molecular weights between 6×10^6 to 23×10^6. In view of these observations it was suggested that in a mixed slurry, anionic polymers would produce selective flocculation of shale while cationics would produce selective coal flocculation; it was considered that the use of non-ionics would achieve little selectivity. In fact in a mixed slurry (50/50 w/w, 5% (w/v)), at near neutral pH, all polymers produced preferential coal flocculation. However products were not necessarily of low ash content, ranging between approximately 32 and 40%. It was suggested that two mechanisms contributed to these high ash values. The first relates to the entrainment which inevitably occurs with

the formation of a three-dimensional floc network, while the second is a result of some affinity of the polyacrylamide towards the shale surface. The latter was minimised with the use of low flocculant dosage levels. The fact that coal appeared to be preferentially flocculated was attributed to various factors namely, hydrophobic bonding by the polymer at non-polar sites on the coal surface, differences in the zeta potentials of coal and shale and the possibility of some differences in the surface properties of a mixed mineral system compared with those of the individual species. In addition, due to the findings of work being conducted in a parallel project within the Mining Department (110), a higher calgon dosage was employed in the selective flocculation tests compared with that in the settling tests; it was felt that this could have contributed considerably to the apparent reduction in shale flocculation. Hydrogen bonding and electrostatic bridge formation are however considered to be the major polymer bonding mechanisms. In the initial selective flocculation tests, a simple beaker decantation method of separation was utilised, but proved rather basic, hence a separating funnel was obtained for use in all further testwork; results indicated that improved separations could be achieved with its use. Due to the wide variation of both polymer molecular weight and ionic character, it was concluded that in these initial tests, it was not possible to isolate any effects of polymer characteristics. As such a range of polymers of constant ionic character and varying molecular weights were obtained for later testwork.

The zeta potentials of separate coal and shale slurries were determined at various pH levels between 2 and 11 and the results

indicated that, over the whole pH range, the zeta potentials of both coal and shale were negative, i.e. the isoelectric point was not achieved. It was considered that this may be a reflection of the presence of calgon, which may increase the negative surface charge. In addition coal samples had been prepared some time previously and as such may have become oxidised to some extent; this would also increase the magnitude of the negative zeta potential. However, the zeta potential of shale over the whole pH range was always of a higher negative value than that of coal, indicating an increased number of charged sites on the surface. At near neutral pH the difference was approximately 11 mV and indicated increased charge density at the shale surface with a corresponding increase in repulsion between shale particles; thus polymer adsorption and/or bridging may be inhibited and result in preferential adsorption at the coal surface. Since zeta potential measurements and selective flocculation tests were conducted at a calgon dosage of 0.5 kg/tonne this may have induced a higher negative value than might have been obtained at 0.08 kg/tonne, and could have also influenced flocculating ability. Combined with previous suggestions, these factors are thought to account for the preferential flocculation of the coal. The effect of pH on the efficiency and selectivity of flocculation was studied and related to the corresponding zeta potentials of the individual minerals, and to the conformational changes which occur in the polymer solution. The results indicated that in general for all types of polymer little selectivity was apparent at low pH, while at high pH reduced flocculation of both minerals occurred. Anionic polymers were found to be particularly susceptible to pH variation, with their ionicity apparently influencing the degree of adsorption.

Optimum results were however achieved at a pH of approximately 6.5 with all polymers and thus all further work was conducted at this level.

Solids concentration is inevitably an important factor in selective flocculation, since too high a level produces excess gangue entrainment, while too low a concentration does not allow sufficient particle contact. To date tests had been conducted at 5% (w/v), a figure typical of froth flotation feed material, and indeed results indicated that this provided optimum conditions.

The use of a promoter prior to flocculant addition, indicated that increased selectivity towards the coal surface could be achieved by increasing its hydrophobicity; thus also improved efficiency. However, the flocs were still weak and minimum ash contents of only about 32% could be obtained.

Six essentially non-ionic and six 50% anionic polymers of molecular weights between 1.8 to 20 x 10^6 were obtained in order that uncertainties regarding the effects of molecular weight and ionic character on both conventional and selective flocculation might be removed. Settling tests were again conducted,but at both low (0.08 kg/tonne) and high (0.5 kg/tonne) calgon dosage levels. From these it was generally concluded that the settling velocities of both coal and shale were increased with an increase in polymer molecular weight; this effect being more pronounced with the anionics. The ionic character and dosage of the polymer and dispersant dosage both influenced the settling velocities of shale. This was the result of a combination of the polymer anionicity and the magnitude of the shale zeta

potential. In general, due to excess surface/polymer repulsion, with the anionics at high calgon dosage shale flocculation was greatly reduced; this occurred regardless of polymer dosage. However, with the non-ionics, although not as extended in solution, bonding mechanisms apparently overcame increases in zeta potentials more easily, especially at high polymer dosage levels. On the other hand coal settling velocities were not affected significantly by an increase in dispersant dosage only, as expected, by an increase in polymer concentration.

Since previous selective flocculation trials, at near neutral pH, had indicated preferential coal flocculation there was no reason to anticipate that these polymers would produce any unexpected results. However it was anticipated that dispersant dosage would be an important factor with respect both to selectivity and efficiency; in fact it was found to be the major contributing factor. At low (0.08 kg/tonne) calgon dosage shale was not effectively dispersed and as such was flocculated in addition to coal, but due to reduced polymer adsorption and/or bridging at the higher dispersant level (0.5 kg/tonne) shale flocculation was decreased. An increase in coal sediment weight at low calgon dosage was considered to be a result of its entrapment within the shale flocs produced rather than any increase in its degree of flocculation. Polymer molecular weight was found to have little effect, with the exception of one anionic polymer which appeared to possess reduced flocculating ability. Similarly, polymer dosage exhibited only a marginal effect when employing non-ionics and very little influence with the anionics.

Finally, further tests were conducted into the effect of preconditioning using oleic acid and creosote. The results suggested that both shale entrainment and some non-specific adsorption of polymer remained a problem even in the presence of a promoter. In addition some coal flotation and loss of polymer flocculating ability was also apparent. Thus only marginal increases in selectivity and efficiency could be achieved and minimum sediment ash contents remained unacceptably high at around 30%. Throughout this work it had also been found that any attempt to remove entrained shale by even the gentlest agitation lead to floc breakdown and resulted in a loss of selectivity, since the flocs would not reform.

To conclude therefore it has been shown that it is technically possible to preferentially flocculate coal from a coal/shale slurry using polyacrylamide polymers. However, no combination of reagents and/or physical conditions results in a product ash of lower than 30% and due to the weak nature of the flocs multistage treatment is not possible.

6.2 RECOMMENDATIONS FOR FUTURE WORK

Although few tests were conducted using cationic polymers or polymers of low anionicity it is considered that similar results would have been obtained i.e. by optimising conditions ash contents of 30% may have been possible but, due to entrainment of shale and some affinity of the polyacrylamides for shale, products below this level would not have been feasible. It is suggested that to overcome this problem it would be necessary to employ a polymer which has no affinity towards the shale surface. This might be achieved by the

use of organic, water insoluble polymers dissolved in either a suitable organic solvent, or a surfactant solution, possibly in conjunction with additional modification of the coal surface to achieve increased hydrophobicity. Although such polymers do not generally possess the same flocculating power as the high molecular weight polyacrylamides it is suggested that, once absolute selectivity is achieved, dosage levels would be less critical and hence much stronger flocs may be produced. Increased shear rates could then be employed which in turn could significantly reduce shale entrainment. In addition, the stronger flocs produced would be more likely to withstand pumping and multistage treatment; elutriation separation, designed to remove any entrained material which may be present, would also be a possibility. It is also considered that hydrophobic polymers may have an application in the area of coal dewatering, since increased surface hydrophobicity leads to enhanced dewatering.

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APPENDICES

APPENDIX 1

COULTER COUNTER DATA SHEETS

COMPLETE TECHNIQUE

INDUSTRIAL MODEL D

COULTER COUNTER DATA AND WEIGHT CONVERSION

Sample: Coal (1) | Source: Bentinck | Electrolyte: Isoton | Dispersant: Nonidet P.42+Ultrasonics (2 mins) | Date: 1.7.81

Aperture Diameter: 140 µm/50 µm | Manometer Volume: 0.5 ml/0.05 ml | Calibration Factor, k: 9.645/3.832 | Calibration Data: 15 µm t = 14.25 I = 0.066 A = 4 | Operator: L.S.

Aperture Resistance: | Coincidence Factor, P: 6.86/3.125 | Notes: t = 15 I = 1 A = 4

t	I	A	n' (raw counts)				$\bar{n}'$	$n'' = P\left(\frac{\bar{n}'}{1000}\right)^2$	B	$n = \bar{n}' + n'' - B$	V = t.I.A	$d = k.\sqrt[3]{V}$ (µm)
20	1	8	0	0	1 0	0 0	0.17			0.17	160	52.4
20	0.5	8	0	0	1 1	3 4	2.25			2.25	80	41.6
20	0.25	8	9		11	10 14	11			11	40	33.0
20	0.13	8	21		34	34 29	29.5			30	20.8	26.5
20	0.066	8	80		67	68 69	71		1	70	10.56	21.2
20	0.033	8	114		137		125		3	123	5.28	16.8
20	0.017	8	275		269		272	0.5	7	266	2.72	13.5
20	0.017	4	503		489		496	1.7	10	488	1.36	10.7
20	0.017	2	893		891		892	5	18	879	0.68	8.48
20	0.017	1	1625		1619		1622	18	25	1615	0.34	6.73
20	0.0093	1	2649		2725		2687	50	21	2716	0.186	5.51
20	0.0053	1	4398		4251		4325	128	38	4415	0.106	4.56
10	0.0053	1	6370		6466		6418	282	50	6650	0.053	3.62
10	0.0033	1	9257		9164		9211	582	68	9725	0.033	3.09
										x 9.65 (factor)		
20	0.017	1	1006		1031	9960 9884	1019	3	16	10287	0.0212	2.67
20	0.0093	1	1533		1488	14520 14544	1521	7	29	14465	0.0117	2.19
20	0.0053	1	1972		2033		2003	13	42	19049	0.0066	1.81
10	0.0053	1	2842		2783		2813	24	100	26412	0.0033	1.44
10	0.0033	1	3789		3656		3723	43	162	34778	0.0021	1.23

Δn	$\bar{V}$	Δn.$\bar{V}$	Σ(Δn)$\bar{V}$	Wt %
0.17	240	41	41	0.77
2.08	120	250	291	5.48
8.75	60	525	816	15.4
18.5	30.4	562	1378	26.0
40	15.68	627	2005	37.7
53	7.92	420	2425	45.7
143	4.00	572	2997	56.4
222	2.04	453	3450	64.9
391	1.02	399	3849	72.5
736	0.51	375	4224	79.5
1101	0.263	290	4514	85.0
1699	0.146	248	4762	89.6
2235	0.0795	178	4940	93.0
3075	0.043	132	5072	95.5
562	0.0271	15	5087	95.8
4178	0.0165	69	5156	97.1
4584	.00915	42	5198	97.9
4363	.00495	36	5234	98.5
8366	.0027	23	5251	98.9
Assume 5312 = 100%				

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COMPLETE TECHNIQUE

INDUSTRIAL MODEL D

COULTER COUNTER DATA AND WEIGHT CONVERSION

Sample: Coal (2) | Source: Bentinck | Electrolyte: Isoton | Dispersant: Nonidet P.42+Ultrasonics (2 mins) | Date: 2.7.81

Aperture Diameter: 140 µm/50 µm | Manometer Volume: 0.5 ml/0.05 ml | Calibration Factor, k: 9.645/3.832 | Calibration Data: 15 µm t = 14.25 I = 0.066 A = 4 | Operator: I.S.

Aperture Resistance: | Coincidence Factor, P: 6.86/3.125 | Notes: t = 15 I = 1 A = 4

t	I	A	n' (raw counts)				$\bar{n}'$	$n'' = P\left(\frac{\bar{n}'}{1000}\right)^2$	B	$n = \bar{n}' + n'' - B$	V = t.I.A	$d = k.\sqrt[3]{V}$ (µm)
20	1	8	0 1	0 0	1 0		0.33			0.33	160	52.4
20	0.5	8	5 3	3 3	5 4		3.8			3.8	80	41.6
20	0.25	8	14	6	7	6	8.25			8	40	33.0
20	0.13	8	29	33	30	35	32			32	20.8	26.5
20	0.066	8	87	76	78	73	79		1	78	10.56	21.2
20	0.033	8	158	144			151		3	148	5.28	16.8
20	0.017	8	277	289			283	1	7	277	2.72	13.5
20	0.017	4	557	565			561	2	10	553	1.36	10.7
20	0.017	2	1012	970			991	7	18	980	0.68	8.48
20	0.017	1	1679	1631			1655	19	25	1649	0.34	6.73
20	0.0093	1	2817	2736			2777	53	21	2809	0.186	5.51
20	0.0053	1	4616	4536			4576	144	38	4682	0.106	4.56
10	0.0053	1	7459	7102			7281	364	50	7595	0.053	3.62
10	0.0033	1	10885	10696			10791	799	68	11522	0.033	3.09
										x factor		
20	0.0093	1	2073	2017			2045	13	29	19580	0.0117	2.19
20	0.0053	1	2976	2851			2914	26	42	27961	0.0066	1.81
10	0.0053	1	4380	4388			4384	60	100	41920	0.0033	1.44
10	0.0033	1	5563	5100			5632	99	162	53736	0.00212	1.23

Δn	$\bar{V}$	Δn.$\bar{V}$	Σ(Δn)$\bar{V}$	Wt.%
0.33	240	79	79	1.3
3.47	120	416	495	8.2
4.45	60	267	762	12.6
24	30.4	730	1492	24.8
46	15.68	721	2213	36.8
70	7.92	554	2767	46.0
129	4.00	516	3283	54.6
276	2.04	563	3846	64.0
427	1.02	436	4282	71.2
669	0.51	341	4623	76.9
1160	0.263	305	4928	82.0
1873	0.146	273	5201	86.5
2913	0.0795	231	5432	90.3
3927	0.043	169	5601	93.1
8058	0.02235	180	5781	96.1
8381	0.00985	77	5858	97.4
13959	0.00495	69	5927	98.6
11816	0.0027	32	5959	99.1
	Assume 6013 = 100%			

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COMPLETE TECHNIQUE

INDUSTRIAL MODEL D

COULTER COUNTER DATA AND WEIGHT CONVERSION

Sample: Coal (3) | Source: Bentinck | Electrolyte: Isoton | Dispersant: Nonidet P.42+Ultrasonics (2 mins) | Date: 2.7.81

Aperture Diameter: 140 µm/50 µm | Manometer Volume: 0.5 ml/0.05 ml | Calibration Factor, k: 9.645/3.832 | Calibration Data: 15 µm t = 14.25 I = 0.066 A = 4 | Operator: L.S.

Aperture Resistance: | Coincidence Factor, P: 6.86/3.125 | Notes: t = 15 I = 1 A = 4

t	I	A	n' (raw counts)				$\bar{n}'$	$n'' = P\left(\frac{\bar{n}'}{1000}\right)^2$	B	$n = \bar{n}' + n'' - B$	V = t.I.A	$d = k.\sqrt[3]{V}$ (µm)
20	0.5	8	1 2	4 2	2 2		2.2			2.2	80	41.6
20	0.25	8	16	12	13	11	13			13	40	33.0
20	0.13	8	42	26	47	35	37.5			38	20.8	26.5
20	0.066	8	103	90			97		1	96	10.56	21.2
20	0.033	8	160	159			160		3	157	5.28	16.8
20	0.017	8	327	329			328	1	7	322	2.72	13.5
20	0.017	4	599	621			610	3	10	603	1.36	10.7
20	0.017	2	1071	1068			1070	8	18	1060	0.68	8.48
20	0.017	1	1852	1803			1828	23	25	1826	0.34	6.73
20	0.0093	1	3174	3109			3142	68	21	3188	0.186	5.51
20	0.0053	1	4906	4831			4869	162	38	4993	0.106	4.56
10	0.0053	1	7281	7559			7420	378	50	7748	0.053	3.62
10	0.0033	1	10621	10689			10676	782	68	11390	0.033	3.07
										x factor		
20	0.017	1	1292	1211			1251	5	16	11966	0.0212	2.67
20	0.0093	1	1826	1805			1815	10	29	17331	0.0117	2.19
20	0.0053	1	2608	2437			2522	20	42	24125	0.0066	1.81
10	0.0053	1	3572	3641			3607	41	100	34238	0.0033	1.44
10	0.0033	1	4653	4699			4676	68	162	44216	0.00212	1.23

Δn	$\bar{V}$	Δn.$\bar{V}$	$\Sigma(\Delta n)\bar{V}$	Wt.%
2.2	120	264	264	4.09
10.8	60	648	912	14.1
24.5	30.4	745	1657	25.7
58	15.68	909	2566	39.8
61	7.92	483	3049	47.3
166	4.0	664	3713	57.6
281	2.04	573	4286	66.5
457	1.02	466	4752	73.8
766	0.51	391	5143	79.9
1362	0.263	358	5501	85.4
1805	0.146	264	5765	89.5
2755	0.0795	219	5984	92.9
3642	0.043	157	6141	95.3
576	0.0271	16	6157	95.6
5365	0.0165	88	6245	96.9
6794	.00915	62	6307	97.9
10113	.00495	50	6357	98.7
9978	0.0027	27	6384	99.1
	Assume 6441 = 100%			

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COMPLETE TECHNIQUE

INDUSTRIAL MODEL D

COULTER COUNTER DATA AND WEIGHT CONVERSION

Sample: Shale (1) | Source: Bentinck | Electrolyte: Isoton | Dispersant: Nonidet P.42+Ultrasonics (2 mins) | Date: 3.7.81

Aperture Diameter: 140 µm/50 µm | Manometer Volume: 0.5/0.05 | Calibration Factor, k: 9.645/3.832 | Calibration Date: 15 µm t = 14.25 I = 0.066 A = 4 | Operator: L.S.

Aperture Resistance: | Coincidence Factor, P: 6.86/3.125 | Notes: t = 15 I = 1 A = 4

t	I	A	n' (raw counts)				$\bar{n}'$	$n'' = P\left(\frac{\bar{n}'}{1000}\right)^2$	B	$n = \bar{n}' + n'' - B$	V = t.I.A	$d = k.\sqrt[3]{V}$ (µm)
20	0.5	8	0 0	0 0	0 0		0			0	80	41.6
20	0.25	8	4 3	2 5	2 3		3.2			3.2	40	33.0
20	0.13	8	12 10	19 10	12 10		12.1			12.1	20.8	26.5
20	0.066	8	23	24	38	26	27.8		1	26.8	10.56	21.2
20	0.033	8	61	61	63	65	62.5		3	59.5	5.28	16.8
20	0.017	8	165	159			162		7	155	2.72	13.5
20	0.017	4	346	338			342	1	10	333	1.36	10.7
20	0.017	2	635	676			656	2	18	640	0.68	8.48
20	0.017	1	1339	1379			1359	10	25	1344	0.34	6.73
20	0.0093	1	2300	2355			2329	36	21	2344	0.186	5.51
20	0.0053	1	4444	4456			4450	137	38	4549	0.106	4.56
10	0.0053	1	7151	7187			7164	404	50	7518	0.053	3.62
10	0.0033	1	13221	13284			13253	1310	68	14495	0.033	3.09
										x factor		
20	0.0093	1	2310	2317			2314	25	29	23399	.0117	2.19
20	0.0053	1	4520	4546			4533	78	42	44273	.0066	1.81
10	0.0053	1	8499	8526			8513	309	100	85485	.0033	1.44
10	0.0033	1	13087	13135			13111	768	162	134374	.0021	1.23

Δn	$\bar{V}$	Δn.$\bar{V}$	Σ(Δn)$\bar{V}$	Wt %
3.2	60	192	192	4.23
8.9	30.4	271	463	10.2
14.7	15.68	231	694	15.3
32.7	7.92	259	953	21.0
95	4	380	1333	29.4
178	2.04	363	1696	37.4
307	1.02	313	2009	44.3
704	0.51	359	2368	52.2
1000	0.263	263	2631	58.0
2205	0.146	322	2953	65.1
2969	0.0795	236	3180	70.3
6977	0.043	300	3489	76.9
8904	.02235	199	3688	81.3
20874	.00915	191	3879	85.5
41212	.00495	204	4083	90.0
48889	0.0027	132	4215	92.9
	Assume	4538 =	100%	

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COMPLETE TECHNIQUE

INDUSTRIAL MODEL D

COULTER COUNTER DATA AND WEIGHT CONVERSION

Sample: Shale (2) | Source: Bentinck | Electrolyte: Isoton | Dispersant: Nonidet P.42+Ultrasonics (2 mins) | Date: 3.7.81

Aperture Diameter: 140 µm/50 µm | Manometer Volume: 0.5/0.05 | Calibration Factor, k: 9.645/3.832 | Calibration Data: 15 µm t = 14.25 I = 0.066 A = 4 | Operator: L.S.

Aperture Resistance: | Coincidence Factor, P: 6.86/3.125 | Notes: t = 15 I = 1 A = 4

t	I	A	n' (raw counts)				$\bar{n}'$	$n'' = P\left(\frac{\bar{n}'}{1000}\right)^2$	B	$n = \bar{n}' + n'' - B$	V = t.I.A	$d = k.\sqrt[3]{V}$ (µm)
20	1	8	0 0	0 0	0 0		0			0	160	52.4
20	0.5	8	0 1	0 1	1 0		0.5			0.5	80	41.6
20	0.25	8	4 6	4 2	3 2		3.5			3.5	40	33.0
20	0.13	8	15	16	14	17	15.5			15.5	20.8	26.5
20	0.066	8	25	35	43	40	36		1	35	10.56	21.2
20	0.033	8	85	91	87		88		3	85	5.28	16.8
20	0.017	8	161	181			171		7	164	2.72	13.5
20	0.017	4	361	352			357	1	10	348	1.36	10.7
20	0.017	2	694	671			683	3	18	668	0.68	8.48
20	0.017	1	1331	1407			1389	13	25	1357	0.34	6.73
20	0.0093	1	2678	2656			2667	49	21	2695	0.186	5.51
20	0.0053	1	5038	5055			5047	175	38	5184	0.106	4.56
10	0.0053	1	8802	8773			8788	530	50	9268	0.053	3.62
10	0.0033	1	15640	15363			15502	1648	68	17082	0.033	3.09
20	0.0093	1	3308	2882			3145	31	29	30369	0.0117	2.19
20	0.0053	1	5938	5735			5837	106	42	56940	0.0066	1.81
10	0.0053	1	10717	10803			10760	362	100	106362	0.0033	1.44
10	0.0033	1	16809	17079			16944	897	162	170602	0.0021	1.23

Δn	$\bar{V}$	Δn.$\bar{V}$	$\Sigma(\Delta n)\bar{V}$	Wt.%
0	240	0	0	
0.5	120	60	60	1.12
3.0	60	180	240	4.48
12.0	30.4	365	605	11.3
19.5	15.68	299	904	16.9
50	7.92	397	1301	24.3
79	4	317	1618	30.2
184	2.04	375	1993	37.2
320	1.02	326	2319	43.3
689	0.51	332	2671	48.9
1338	0.263	352	3023	56.4
2489	0.146	363	3386	63.3
4084	0.0795	325	3711	69.3
7814	0.043	336	4047	75.6
13287	.02235	297	4344	81.2
26571	.00915	243	4587	85.7
49422	.00495	245	4832	90.6
64260	0.0027	173	5005	93.5
	Assume 5353 = 100%			

9942047

COMPLETE TECHNIQUE

INDUSTRIAL MODEL D

COULTER COUNTER DATA AND WEIGHT CONVERSION

Sample: Shale (3) | Source: Bentinck | Electrolyte: Isoton | Dispersant: Nonidet P.42+Ultrasonics (2 mins) | Date: 6.7.81

Aperture Diameter: 140 µm/50 µm | Manometer Volume: 0.5/0.05 | Calibration Factor, k: 9.645/3.832 | Calibration Data: 15 µm t = 14.25 I = 0.066 A = 4 | Operator: L.S.

Aperture Resistance: | Coincidence Factor, P: 6.86/3.125 | Notes: t = 15 I = 1 A = 4

t	I	A	n' (raw counts)				$\bar{n}'$	$n'' = P\left(\frac{\bar{n}'}{1000}\right)^2$	B	$n = \bar{n}' + n'' - B$	V = t.I.A	$d = k.\sqrt[3]{V}$ (µm)
20	1	8	0 0	0 0	0 0		0			0	160	52.4
20	0.5	8	2 1	1 0	0 2		1			1	80	41.6
20	0.25	8	5 7	9 5	3 5		6			6	40	33.0
20	0.13	8	10	15	14	14	13.3			13.3	20.8	26.5
20	0.066	8	30	40	40	31	35.3		1	34.3	10.56	21.2
20	0.033	8	93	80	89		87.3		3	84.3	5.28	16.8
20	0.017	8	170	174			172		7	165	2.72	13.5
20	0.017	4	364	354			359	1	10	350	1.36	10.7
20	0.017	2	662	660			661	4	18	647	0.68	8.48
20	0.017	1	1298	1314			1306	15	25	1296	0.34	6.73
20	0.0093	1	2759	2764			2762	53	21	2794	0.186	5.51
20	0.0053	1	5111	5147			5129	182	38	5273	0.108	4.46
10	0.0033	1	9388	9434			9411	528	50	9889	0.053	3.62
10	0.0053	1	15888	15913			15930	1585	68	17447	0.033	3.09
										x factor		
20	0.0093	1	3210	3218			3214	25	29	31496	0.0117	2.19
20	0.0053	1	5322	5381			5351	74	42	52480	0.0066	1.81
10	0.0053	1	11260	11284			11272	295	100	110662	0.0033	1.44
10	0.0033	1	16420	16510			16465	575	162	161773	0.0021	1.23

Δn	$\bar{V}$	Δn.$\bar{V}$	$\Sigma(\Delta n)\bar{V}$	Wt.%
1	120	128	120	2.25
5	60	318	438	8.82
7.3	30.4	222	660	12.4
21	15.68	330	990	18.6
50	7.92	394	1384	26.0
81	4	325	1709	32.1
185	2.04	378	2087	39.2
297	1.02	303	2390	44.9
649	0.51	331	2721	51.1
1498	0.263	394	3115	58.5
2479	0.146	362	3477	65.3
4616	0.0795	367	3844	72.2
7558	0.043	325	4169	78.3
14049	.02235	314	4483	84.2
20984	.00915	192	4675	87.8
58182	.00495	288	4963	93.2
51111	0.0027	138	5101	95.8
	Assume	5325	= 100%	

9942047

APPENDIX 2

SETTLING RATES AND SUPERNATANT CLARITIES OF COAL AND SHALE

APPENDIX 2

(a) Settling Rates ($ms^{-1} \times 10^{-3}$) of Shale Using High Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)				
	0.025	0.050	0.10	0.20	0.30
A6	9.1	13.4	12.7	17.9	16.5
A5	6.1	6.33	8.27	15.4	23.9
A4	12.2	13.4	18.3	17.9	22.2
A3	8.4	8.7	8.07	9.09	14.3
A2	1.9	3.64	8.60	21.5	35.8
A1	< 1	2.69	3.12	18.0	35.8
N.I.	< 1	2.56	2.91	3.58	5.97
C1	< 1	< 1	2.60	2.95	3.54
C2	< 1	< 1	< 1	2.91	2.98
C3	< 1	< 1	< 1	2.47	2.30
C4	< 1	< 1	< 1	1.05	< 1

(b) Settling Rates ($ms^{-1} \times 10^{-3}$) of Shale Using Medium Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)				
	0.025	0.050	0.10	0.20	0.30
A10	1.00	1.63	1.85	1.75	3.57
A9	3.12	3.71	4.30	4.78	5.56
A8	6.20	7.68	7.69	7.69	9.09
A7	1.10	2.76	5.65	14.3	12.7
C5	< 1	< 1	1.00	2.98	3.03
C6	< 1	< 1	1.44	1.65	1.51
C7	< 1	< 1	< 1	1.00	1.10
C8	< 1	< 1	< 1	1.14	1.04

(c) Settling Rates ($ms^{-1} \times 10^{-3}$) of Coal Using High Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)				
	0.025	0.050	0.10	0.20	0.30
A6	1.50	1.61	1.80	4.00	3.85
A5	1.61	1.69	1.75	1.95	2.70
A4	1.65	1.80	2.93	4.00	4.33
A3	1.82	1.92	2.13	1.92	2.00
A2	1.72	2.00	2.04	2.17	2.27
A1	1.92	2.44	3.57	3.70	2.94
N.I.	1.70	1.96	2.44	3.45	3.70
C1	1.95	2.22	2.63	3.45	3.85
C2	1.82	1.96	2.56	3.03	3.33
C3	< 1	1.30	1.39	1.67	1.79
C4	1.20	1.53	2.00	1.92	2.13

(d) Settling Rates ($ms^{-1} \times 10^{-3}$) of Coal Using Medium Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)				
	0.025	0.050	0.10	0.20	0.30
A10	< 1	< 1	1.08	1.58	1.85
A9	1.0	1.33	1.61	1.66	1.75
A8	1.45	1.52	1.47	1.79	2.22
A7	1.25	1.74	1.92	1.92	2.00
C5	1.28	1.56	2.05	2.17	1.90
C6	< 1	1.18	1.22	1.72	1.79
C7	1.40	1.42	1.28	1.16	1.13
C8	1.0	1.28	1.61	1.83	1.92

(e) Settling Rates ($ms^{-1} \times 10^{-3}$) of Coal Using High Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)				
	0.025	0.050	0.10	0.20	0.30
S	1.90	1.94	2.72	2.38	2.58
T	1.78	1.78	1.97	2.34	2.58
U	2.05	2.17	2.44	2.32	2.63
V	1.92	1.92	2.12	2.78	2.78
W	1.92	2.17	2.63	2.70	2.38
X	1.80	1.88	2.02	2.27	2.44
Y	1.78	1.63	1.92	2.38	2.63
Z	1.63	1.69	1.81	2.22	2.78

(f) Settling Rates ($ms^{-1} \times 10^{-3}$) of Shale Using High Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)			
	0.050	0.10	0.20	0.30
S	< 1	3.0	4.20	6.55
T	< 1	6.67	6.45	8.00
U	2.53	37.7	10.0	36.7
V	9.52	18.2	26.9	33.3
W	16.5	23.9	26.9	25.0
X	14.3	16.5	27.0	26.9
Y	11.1	12.5	14.7	15.7
Z	6.94	8.08	11.6	13.8

(g) Supernatant Clarity of Flocculated Coal Slurries Using High Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)				
	0.025	0.050	0.10	0.20	0.30
A6	2	2	2	3	3
A5	4	3	3	2	3
A4	2	2	2	2	2
A3	4	3	3	2	2
A2	5	2	2	2	2
A1	3	2	2	2	1
N.I.	2	2	2	2	1
C1	3	2	2	1	1
C2	5	2	1	1	1
C3	5	3	3	2	2
C4	5	5	5	3	2

(h) Supernatant Clarity of Flocculated Shale Slurries Using High Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)				
	0.025	0.050	0.10	0.20	0.30
A6	5	5	5	3	3
A5	5	5	3	3	3
A4	5	5	3	3	3
A3	5	5	3	3	3
A2	5	4	3	2	2
A1	6-	6	6	2	1
N.I.	6-	6	6	5	5
C1	6-	6-	6	5	5
C2	6-	6-	6	6	6
C3	6-	6-	6-	6	6
C4	6-	6-	6-	6-	6-

Increasing Supernatant Clarity →

6 — Very Cloudy — Large mass of solids remaining in suspension

1 — Clear — Little solid remaining in suspension

(i) Supernatant Clarity of Flocculated Coal Slurries with Medium Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)				
	0.025	0.050	0.10	0.20	0.30
A10	5	5	5	5	5
A9	5+	5+	5+	5+	5+
A8	4	4	4	3	3
A7	4	4	4	3	3
C5	4	3	2	1	2
C6	5	5	5	3	2
C7	5	4	3	1	1
C8	5	5	4	4	4

(j) Supernatant Clarity of Flocculated Shale Slurries with Medium Molecular Weight Polymers.

Polymer Identification	Polymer Dosage (kg/tonne)				
	0.025	0.050	0.10	0.20	0.30
A10	5	5	5	5	5
A9	5	4	3	3	3
A8	5	5	5	5	5
A7	6	5	4	3	3
C5	6	6	6	6	5
C6	6	6	6	6	6
C7	6	6	6	6	6
C8	6	6	6	6	6

Increasing Supernatant Clarity

6 ⟶ 1

Very Cloudy — Clear

Large mass of solids remaining in suspension

Little solid remaining in suspension

APPENDIX 3

INITIAL SELECTIVE FLOCCULATION TRIALS

APPENDIX 3

High Molecular Weight Polymers

(a) Polymer Dosage = 0.005 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A6	39.5	81.6	91.4
A5	38.7	82.0	93.1
A4	39.8	83.2	92.8
A3	37.4	74.4	86.2
A2	37.6	75.0	86.7
A1	38.7	54.6	62.0
N.I.	34.2	67.2	81.9
C1	34.2	65.4	79.8
C2	34.8	58.4	70.6
C3	34.3	63.6	77.4
C4	35.5	67.6	80.7

(b) Polymer Dosage = 0.01 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A6	40.0	85.4	95.0
A5	40.0	84.6	94.0
A4	42.6	88.8	94.4
A3	39.9	81.2	92.2
A2	40.3	82.2	90.9
A1	39.2	68.4	77.0
N.I.	35.3	70.6	84.7
C1	34.8	67.6	81.6
C2	35.3	62.8	75.2
C3	34.4	66.8	81.2
C4	35.3	70.0	83.9

(c) Polymer Dosage = 0.015 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A6	40.8	87.8	96.3
A5	41.3	87.4	95.1
A4	43.1	92.4	97.4
A3	40.1	82.4	91.5
A2	39.9	86.6	96.5
A1	40.2	75.2	83.3
N.I.	35.7	72.2	86.0
C1	35.1	69.0	82.9
C2	36.8	72.6	85.0
C3	35.2	70.4	84.5
C4	35.6	66.4	79.2

(d) Polymer Dosage = 0.025 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A6	42.2	89.8	96.2
A5	42.1	88.8	95.2
A4	43.3	90.0	94.6
A3	42.1	87.8	94.2
A2	40.8	90.0	98.8
A1	42.2	92.0	98.5
N.I.	36.9	74.6	87.2
C1	36.4	69.0	81.3
C2	37.6	74.2	85.7
C3	35.7	72.6	86.5
C4	36.2	63.6	75.2

(e) Polymer Dosage = 0.050 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A6	39.7	84.6	94.5
A5	40.7	87.0	95.5
A4	42.8	91.6	97.0
A3	41.1	85.0	92.8
A2	43.0	90.4	95.4
A1	42.2	93.0	99.6
N.I.	37.9	75.4	85.4
C1	37.9	73.4	84.5
C2	39.4	79.8	89.6
C3	37.0	73.0	85.2
C4	38.0	69.2	79.5

Medium Molecular Weight Polymers

(f) Polymer Dosage = 0.005 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A10	34.4	64.2	78.1
A9	34.6	69.2	83.8
A8	32.4	69.2	86.6
A7	38.6	75.2	85.6
C5	34.9	67.2	81.3
C6	35.3	66.8	80.0
C7	34.8	58.6	70.8
C8	33.8	67.0	82.1

(g) Polymer Dosage = 0.010 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A10	34.0	65.8	80.5
A9	32.5	68.6	85.8
A8	32.9	71.4	88.7
A7	39.9	81.6	90.8
C5	34.5	68.2	82.8
C6	35.7	67.6	80.5
C7	34.5	67.4	81.7
C8	33.9	65.4	80.1

(h) Polymer Dosage = 0.015 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A10	34.9	65.6	79.1
A9	32.9	66.4	82.5
A8	32.3	72.2	90.5
A7	41.4	85.8	93.1
C5	36.3	67.4	79.5
C6	36.0	70.6	83.7
C7	34.8	69.6	84.1
C8	35.8	69.2	82.3

(i) Polymer Dosage = 0.025 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A10	37.2	75.8	88.2
A9	33.4	67.8	83.6
A8	33.9	72.0	88.1
A7	40.9	86.4	94.6
C5	36.4	72.6	85.6
C6	36.2	71.8	84.9
C7	35.8	66.8	79.5
C8	34.1	64.8	79.1

(j) Polymer Dosage = 0.050 kg/tonne

Polymer	% Ash in Sediment	% Wt. Yield	% Combustible Recovery
A10	34.0	68.0	83.2
A9	33.7	67.6	83.0
A8	33.8	75.4	88.6
A7	42.8	89.0	94.3
C5	38.3	74.8	85.5
C6	37.1	71.4	82.2
C7	37.9	69.2	79.8
C8	36.3	62.8	74.1

APPENDIX 4

ZETA POTENTIAL RESULTS

APPENDIX 4

(a) Zeta Potential Results for Shale at Various pH Values

pH	Average Electrophoretic Velocity (μm/sec)	Mobility ($x10^{-8}$) ($m^2 volt^{-1} sec^{-1}$)	Zeta Potential (mV)
1.9	12.12	2.374	-30.5
2.0	15.79	2.472	-31.7
2.0	14.55	2.278	-29.2
2.0	14.12	2.211	-28.4
2.4	24.13	2.152	-27.6
2.6	26.87	2.338	-30.0
2.7	24.99	2.175	-27.9
3.5	28.49	2.479	-31.8
4.2	28.74	2.501	-32.1
4.5	32.33	2.813	-36.1
5.4	33.40	2.906	-37.3
5.5	37.29	3.244	-41.6
5.6	39.42	3.429	-44.0
6.4	41.31	3.594	-46.1
6.6	41.77	3.634	-46.6
7.1	41.49	3.610	-46.3
7.5	46.51	4.047	-51.9
8.6	41.77	3.634	-46.6
9.3	45.21	3.933	-50.5
10.6	46.71	4.064	-52.1
10.9	47.17	4.104	-52.6

(b) Zeta Potential Results for Coal at Various pH Values

pH	Average Electrophoretic Velocity (μm/sec)	Mobility ($m^2 volt^{-1} sec^{-1}$)	Zeta Potential (mV)
1.9	5.13	1.004×10^{-8}	-12.9
2.0	4.68	4.072×10^{-9}	-5.2
2.5	10.72	9.323×10^{-9}	-12.0
2.7	9.11	7.929×10^{-9}	-10.2
2.95	10.77	9.367×10^{-9}	-12.0
3.1	11.89	1.034×10^{-8}	-13.3
4.2	15.96	1.388×10^{-8}	-17.8
4.4	15.89	1.383×10^{-8}	-17.7
4.8	14.52	1.263×10^{-8}	-16.2
5.3	20.33	1.769×10^{-8}	-22.7
5.45	23.85	2.075×10^{-8}	-26.6
5.5	23.89	2.078×10^{-8}	-26.7
6.45	31.31	2.724×10^{-8}	-34.9
6.5	32.38	2.817×10^{-8}	-36.1
7.3	33.92	2.951×10^{-8}	-37.9
7.6	35.70	3.106×10^{-8}	-39.8
8.4	39.08	3.400×10^{-8}	-43.6
8.6	38.24	3.327×10^{-8}	-42.7
9.5	38.97	3.390×10^{-8}	-43.5
9.6	39.76	3.459×10^{-8}	-44.4
9.7	41.0	3.570×10^{-8}	-45.8
10.7	40.84	3.554×10^{-8}	-44.6
10.8	38.67	3.364×10^{-8}	-43.2

APPENDIX 5

SELECTIVE FLOCCULATION AT VARIOUS pH LEVELS

APPENDIX 5

(a) A6 - 0.005 kg/tonne

pH	% Ash in Sediment	% Weight Yield	% Combustible Recovery	% Ash in Suspension
2.5	46.2	69.8	69.6	45.7
3.4	43.9	67.4	56.7	48.7
4.4	38.6	75.6	86.0	62.3
5.5	35.4	70.6	84.4	79.7
6.3	32.6	61.4	81.2	73.5
7.5	39.0	34.5	39.0	47.7
8.4	41.0	29.2	31.9	44.9
9.5	42.6	27.2	29.0	44.4
10.5	43.7	21.0	22.0	43.9

(b) A6 - 0.01 kg/tonne

pH	% Ash in Sediment	% Weight Yield	% Combustible Recovery	% Ash in Suspension
2.5	46.1	75.4	75.3	43.6
3.4	44.6	87.0	89.4	61.6
4.4	42.1	83.0	89.1	65.9
5.5	37.9	76.2	87.6	81.4
6.3	34.6	68.9	85.1	79.2
7.5	35.3	45.2	54.3	53.7
8.4	45.1	28.9	29.3	45.4
9.5	45.0	29.2	29.8	44.6
10.5	49.9	27.2	25.3	43.6

(c) A6 - 0.015 kg/tonne

pH	% Ash in Sediment	% Weight Yield	% Combustible Recovery	% Ash in Suspension
2.5	45.1	88.8	90.3	59.7
3.4	44.3	87.6	90.4	60.3
4.4	43.7	87.0	90.8	66.8
5.5	39.1	78.8	88.9	75.9
6.3	35.1	66.6	83.7	77.0
7.5	41.3	40.3	43.8	49.6
8.4	43.5	41.2	43.1	46.0
9.5	42.2	32.5	34.8	44.2
10.5	43.8	34.4	29.0	44.7

(d) N.I. - 0.010 kg/tonne

pH	% Ash in Sediment	% Weight Yield	% Combustible Recovery	% Ash in Suspension
2.5	41.0	81.0	88.7	61.1
3.5	40.2	69.2	76.7	55.2
4.5	40.0	61.2	68.0	66.4
5.5	36.4	72.0	84.9	70.9
6.5	34.7	68.6	83.0	71.1
7.6	32.3	62.8	78.8	66.4
8.6	30.9	33.6	43.2	49.2
9.6	34.2	45.2	55.2	49.6
10.7	35.1	47.9	57.6	52.6

(e) C1 - 0.010 kg/tonne

pH	% Ash in Sediment	% Weight Yield	% Combustible Recovery	% Ash in Suspension
2.6	42.4	87.4	93.3	62.5
3.6	42.1	73.2	78.0	44.3
4.6	38.5	60.3	68.7	53.4
5.4	37.5	74.6	86.3	72.7
6.7	32.4	70.0	88.9	75.0
7.9	32.6	49.5	86.8	57.4
8.6	31.6	40.4	51.2	52.5
9.8	36.0	54.0	64.1	56.8
10.6	32.9	46.3	57.6	54.2

(f) A8 - 0.005 kg/tonne

pH	% Ash in Sediment	% Weight Yield	% Combustible Recovery	% Ash in Suspension
2.5	45.3	92.0	93.1	55.1
3.5	43.9	82.2	85.4	51.0
4.4	43.1	86.3	91.0	64.8
5.5	35.2	73.6	88.5	73.7
6.4	31.3	66.5	84.6	77.6
7.7	37.6	44.6	51.5	49.1
8.5	39.9	32.0	35.7	45.7
9.5	46.1	23.8	23.7	43.6
10.6	44.8	20.5	21.0	43.6

(g) A8 - 0.010 kg/tonne

pH	% Ash in Sediment	% Weight Yield	% Combustible Recovery	% Ash in Suspension
2.5	45.5	92.1	93.0	53.5
3.5	45.5	63.0	91.0	45.1
4.4	43.1	85.8	90.5	65.9
5.5	39.1	76.1	85.9	71.8
6.4	31.5	64.2	84.5	76.3
7.7	44.7	27.0	27.6	45.3
8.5	47.6	20.0	19.4	43.7
9.5	45.5	24.0	24.3	44.5
10.6	50.5	19.2	17.6	43.5

(h) A8 - 0.015 kg/tonne

pH	% Ash in Sediment	% Weight Yield	% Combustible Recovery	% Ash in Suspension
2.5	44.6	87.6	89.9	45.8
3.5	44.8	91.8	94.0	64.4
4.4	43.8	88.8	92.4	67.2
5.5	37.8	76.7	88.4	77.3
6.4	32.2	65.5	84.7	77.6
7.7	41.4	23.4	25.5	46.0
8.5	43.1	29.8	31.4	44.9
9.5	46.5	28.4	28.2	43.5
10.6	40.9	32.0	35.0	44.9

(i) C7 - 0.010 kg/tonne

pH	% Ash in Sediment	% Weight Yield	% Combustible Recovery	% Ash in Suspension
2.6	44.2	49.4	51.1	43.1
3.6	44.9	42.6	43.5	43.2
4.7	45.2	34.9	35.4	43.8
5.6	43.6	27.4	28.6	43.6
6.4	41.8	25.8	27.8	44.0
7.7	40.0	42.5	47.2	50.9
8.7	37.8	37.4	43.1	46.7
9.6	43.4	21.4	22.4	43.1
10.7	49.5	30.5	28.5	42.6

(j) A6 - 0.005 kg/tonne

pH	Percentage Shale in Sediment	Wt. Shale in Sediment	Wt. Coal in Sediment
2.5	50.2	17.5	17.4
3.4	47.4	16.0	17.7
4.4	41.0	15.5	22.3
5.5	37.2	13.1	22.2
6.3	33.8	10.4	20.3
7.5	41.5	7.2	10.1
8.4	43.9	6.4	8.2
9.5	45.9	6.2	7.4
10.5	47.4	5.0	5.5

(k) A6 - 0.010 kg/tonne

pH	Percentage Shale in Sediment	Wt. Shale in Sediment	Wt. Coal in Sediment
2.5	50.1	18.9	18.8
3.4	48.3	21.0	22.5
4.4	45.3	18.8	22.7
5.5	40.2	15.3	22.8
6.3	36.2	12.5	21.9
7.5	37.0	8.4	14.2
8.4	48.9	7.1	7.4
9.5	48.8	7.1	7.5
10.5	54.9	7.5	6.1

(ℓ) A6 - 0.015 kg/tonne

pH	Percentage Shale in Sediment	Wt. Shale in Sediment	Wt. Coal in Sediment
2.5	48.9	21.7	22.7
3.4	47.9	21.0	22.8
4.4	47.2	20.5	23.0
5.5	41.6	16.4	23.0
6.3	36.8	12.3	21.0
7.5	44.3	8.9	11.3
8.4	47.0	9.7	10.9
9.5	45.4	7.4	8.9
10.5	47.4	8.1	9.1

(m) N.I. - 0.010 kg/tonne

pH	Percentage Shale in Sediment	Wt. Shale in Sediment	Wt. Coal in Sediment
2.5	43.9	17.8	22.7
3.5	43.0	14.9	19.7
4.5	42.7	13.1	17.5
5.5	38.4	13.8	22.2
6.5	31.8	10.9	23.4
7.6	33.4	10.5	20.9
8.6	31.7	5.3	11.5
9.6	35.7	8.1	14.5
10.7	36.8	8.8	15.2

(n) C1 - 0.010 kg/tonne

pH	Percentage Shale in Sediment	Wt. Shale in Sediment	Wt. Coal in Sediment
2.6	45.6	19.9	23.8
3.6	45.3	16.6	20.0
4.6	40.9	12.3	17.9
5.4	39.7	14.8	22.5
6.7	33.5	11.7	23.3
7.9	33.8	8.4	16.4
8.6	32.6	6.6	13.6
9.8	37.9	10.2	16.8
10.6	34.1	7.9	15.3

(o) A8 - 0.005 kg/tonne

pH	Percentage Shale in Sediment	Wt. Shale in Sediment	Wt. Coal in Sediment
2.5	49.2	22.6	23.4
3.5	47.4	19.5	21.6
4.4	46.5	20.0	23.2
5.5	36.9	13.6	23.2
6.4	32.2	10.7	22.6
7.7	39.8	6.4	9.6
8.5	42.6	6.8	9.2
9.5	50.1	6.0	5.9
10.6	48.5	5.0	5.3

(p) A8 - 0.010 kg/tonne

pH	Percentage Shale in Sediment	Wt. Shale in Sediment	Wt. Coal in Sediment
2.5	49.4	22.7	23.4
3.5	49.4	15.6	15.9
4.4	46.4	19.9	23.0
5.5	41.6	15.8	22.3
6.4	32.4	10.4	21.7
7.7	48.4	6.5	7.0
8.5	51.9	5.2	4.8
9.5	49.4	5.9	6.1
10.6	55.4	5.3	4.3

(q) A8 - 0.015 kg/tonne

pH	Percentage Shale in Sediment	Wt. Shale in Sediment	Wt. Coal in Sediment
2.5	48.3	21.2	22.6
3.5	48.5	22.3	23.6
4.4	47.3	21.0	23.4
5.5	40.1	15.4	23.0
6.4	33.3	10.9	21.9
7.7	44.3	5.2	6.4
8.5	46.4	6.9	8.0
9.5	50.6	7.2	7.0
10.6	43.8	7.0	9.0

(r) C7 - 0.010 kg/tonne

pH	Percentage Shale in Sediment	Wt. Shale in Sediment	Wt. Coal in Sediment
2.6	47.8	11.8	12.9
3.6	48.7	10.4	10.9
4.7	49.0	8.6	8.9
5.6	47.1	6.5	7.2
6.4	44.9	5.8	7.1
7.7	42.7	9.1	12.2
8.7	40.1	7.5	11.2
9.6	46.9	5.6	5.1
10.7	54.2	8.3	7.0

APPENDIX 6

PROMOTER EFFECTS - INITIAL TESTS

APPENDIX 6

(a) Polymer C7 + Oleic Acid

	kg/tonne oleic acid				
	0.5	1	2	3	5
% Ash	34.7	33.1	34.4	31.8	30.7
% Wt. Yield	44.8	46.4	45.4	53.6	57.8
% Combustible Recovery	54.2	57.5	55.2	67.7	74.2
% Shale in Sediment	36.3	34.4	36.0	32.8	31.5
Wt. Shale in Sediment	8.1	9.9	8.2	8.8	9.1
Wt. Coal in Sediment	14.3	13.3	14.5	18.0	19.8

(b) Polymer C7 + Creosote

	kg/tonne creosote				
	0.5	1	2	3	5
% Ash	35.0	36.0	38.0	40.3	44.1
% Wt. Yield	53.6	50.1	49.2	51.8	47.2
% Combustible Recovery	64.0	60.1	56.5	64.1	49.0
% Shale in Sediment	36.7	37.9	40.3	43.1	47.7
Wt. Shale in Sediment	9.8	9.5	9.9	11.2	11.3
Wt. Coal in Sediment	17.0	15.6	14.7	14.7	12.3

(c) Polymer C7 + Diesel Oil

	kg/tonne diesel oil				
	0.4	0.8	2.0	2.8	4.8
% Ash	37.1	34.4	34.7	34.0	35.0
% Wt. Yield	58.2	56.0	60.8	63.6	64.8
% Combustible Recovery	67.8	68.1	73.5	77.8	78.0
% Shale in Sediment	39.2	36.0	36.3	35.5	36.7
Wt. Shale in Sediment	11.4	10.1	11.0	11.3	11.9
Wt. Coal in Sediment	17.7	17.9	19.4	20.5	20.5

APPENDIX 7

SETTLING TESTS USING NEW RANGE OF POLYMER SAMPLES

APPENDIX 7

Settling rate of coal without polymer addition - 0.33 $ms^{-1} \times 10^{-3}$

Settling rate of shale without polymer addition - 0.3 $ms^{-1} \times 10^{-3}$

Non-Ionic Polymers

Dispersant Dosage 0.08 kg/tonne

(a) Settling Rates ($ms^{-1} \times 10^{-3}$) of coal

Polymer	Polymer Dosage (kg/tonne)					
	0.01	0.025	0.05	0.10	0.20	0.30
A	0.37	0.50	0.68	0.88	1.09	1.15
B	0.61	0.91	1.36	1.76	1.83	1.68
C	0.66	1.10	1.62	1.83	1.96	2.29
D	0.65	1.52	1.69	1.81	2.00	2.20
E	0.78	1.46	1.72	1.89	2.46	3.13
F	0.68	1.37	1.57	1.78	2.14	2.41

(b) Settling Rates ($ms^{-1} \times 10^{-3}$) of shale

Polymer	Polymer Dosage (kg/tonne)					
	0.01	0.025	0.05	0.10	0.20	0.30
A	1.1	1.0	1.6	3.0	3.9	5.2
B	1.1	1.2	2.9	3.3	5.0	5.6
C	1.1	1.4	2.6	3.6	4.5	5.3
D	1.2	1.6	2.4	3.2	4.1	14.7
E	1.3	1.6	2.9	4.6	5.0	5.8
F	1.2	1.5	1.6	2.6	4.6	50.0

Dispersant Dosage 0.5 kg/tonne

(c) Settling Rates ($ms^{-1} \times 10^{-3}$) of coal

Polymer	Polymer Dosage (kg/tonne)					
	0.01	0.025	0.05	0.10	0.20	0.30
A	0.35	0.58	0.76	1.04	1.22	1.16
B	0.4	1.00	1.34	1.82	1.77	1.88
C	0.58	1.36	1.61	1.86	2.00	2.00
D	0.53	1.29	1.69	1.87	2.10	2.24
E	1.33	1.67	1.89	2.36	2.54	2.91
F	0.9	1.58	1.83	1.93	2.82	3.72

(d) Settling Rates ($ms^{-1} \times 10^{-3}$) of shale

Polymer	Polymer Dosage (kg/tonne)					
	0.01	0.025	0.05	0.10	0.20	0.30
A	1.0	1.2	1.2	1.9	1.2	1.2
B	1.1	1.3	1.6	2.5	5.7	6.9
C	1.0	1.7	2.4	5.3	6.3	7.5
D	1.2	1.4	2.2	3.6	5.7	6.7
E	1.0	1.5	2.9	3.1	6.1	7.3
F	1.1	1.4	2.0	5.5	7.3	8.3

50% Anionic Polymers

Dispersant Dosage 0.08 kg/tonne

(e) Settling Rates ($ms^{-1} \times 10^{-3}$) of coal

Polymer	Polymer Dosage (kg/tonne)					
	0.01	0.025	0.05	0.10	0.20	0.30
G	0.55	0.76	0.79	1.44	1.64	1.42
H	0.62	1.0	1.39	1.47	1.49	1.79
I	0.71	1.41	1.42	1.46	1.75	2.24
J	0.50	0.68	0.95	1.52	1.49	1.59
K	0.66	1.04	1.52	1.59	1.57	2.09
L	1.03	1.45	1.53	2.4	4.46	5.71

(f) Settling Rates ($ms^{-1} \times 10^{-3}$) of shale

Polymer	Polymer Dosage (kg/tonne)					
	0.01	0.025	0.05	0.10	0.20	0.30
G	<1.0	2.7	4.8	5.0	5.9	6.5
H	1.4	5.9	6.7	7.7	8.0	6.25
I	1.4	6.0	7.8	8.1	7.6	6.25
J	1.1	2.8	2.5	7.4	9.1	6.2
K	2.2	5.3	6.8	6.8	7.4	7.4
L	2.9	5.6	7.8	7.2	6.5	7.1

Dispersant Dosage 0.5 kg/tonne

(g) Settling Rate ($ms^{-1} \times 10^{-3}$) of coal

Polymer	Polymer Dosage (kg/tonne)					
	0.01	0.025	0.05	0.10	0.20	0.30
G	0.54	0.8	1.6	1.83	1.56	1.52
H	0.53	0.83	1.59	1.47	1.69	2.04
I	0.61	1.21	1.64	1.61	2.15	2.70
J	0.66	0.72	1.15	1.83	1.87	2.27
K	0.76	1.23	1.80	1.92	2.49	3.38
L	1.68	1.87	2.18	5.13	7.14	6.67

(h) Settling Rates ($ms^{-1} \times 10^{-3}$) of shale

Polymer	Polymer Dosage (kg/tonne)					
	0.01	0.025	0.05	0.10	0.20	0.30
G	<1.0	1.4	1.25	1.1	<1.0	<1.0
H	<1.0	1.6	1.3	1.3	1.3	1.4
I	<1.0	1.2	1.3	1.3	<1.0	<1.0
J	<1.0	1.3	1.4	1.4	1.5	1.5
K	<1.0	1.5	1.8	1.8	1.5	<1.0
L	<1.0	1.6	3.6	3.6	4.8	1.9

APPENDIX 8

EFFECTS OF COAL PRETREATMENT ON THE SELECTIVITY OF THE SEPARATION PROCESS

APPENDIX 8

Oleic Acid Additions (kg/tonne)

(a) Without Polymer

Oleic Acid Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	42.0	50.0	53.7	13.7	11.3	48.0
0.5	33.3	58.6	72.4	19.2	10.1	65.5
1	31.1	60.6	77.3	20.6	9.7	70.5
2	29.8	61.2	79.6	21.3	9.3	74.7
4	32.6	59.2	73.9	19.6	10.0	66.9
5	36.3	39.6	46.7	12.2	7.6	58.6

(b) Polymer B

Oleic Acid Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	32.5	55.0	68.8	18.2	9.3	63.2
0.5	33.9	54.8	67.1	17.7	9.7	61.0
1	33.6	60.0	73.8	19.5	10.5	64.8
2	30.4	60.0	77.3	20.7	9.3	70.5
4	32.3	62.0	77.8	20.6	10.4	70.3
5	33.2	54.0	66.8	16.3	10.7	61.3

(c) Polymer D

Oleic Acid Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	33.7	56.0	68.8	18.2	9.8	62.7
0.5	34.5	53.0	64.3	15.6	10.9	58.8
1	35.4	54.0	64.6	17.0	10.0	58.9
2	32.0	55.8	70.3	19.0	8.9	66.2
4	31.4	59.2	75.2	20.9	8.7	68.9
5	31.1	54.4	69.4	18.5	8.7	62.1

(d) Polymer F

Oleic Acid Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	33.6	49.0	60.3	15.9	8.6	60.3
0.5	35.2	49.2	59.0	15.5	9.1	57.3
1	32.6	54.4	67.9	18.0	9.2	59.8
2	31.2	58.6	74.7	19.9	9.4	69.9
4	34.1	57.6	70.3	18.5	10.3	65.9
5	35.5	49.0	58.5	13.8	10.7	56.8

(e) Polymer G

Oleic Acid Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	33.2	52.2	64.6	17.1	9.0	59.4
0.5	40.4	33.8	37.3	9.6	7.3	49.0
1	34.1	49.8	59.8	15.8	8.7	58.2
2	30.8	58.0	74.3	19.8	9.2	72.0
4	33.0	52.2	64.8	17.1	9.0	60.5
5	32.8	50.4	62.7	16.6	8.6	61.2

(f) Polymer I

Oleic Acid Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	33.3	47.8	59.0	15.6	8.3	56.3
0.5	34.8	45.2	53.1	14.0	8.0	55.0
1	34.0	44.6	54.5	14.4	7.9	57.7
2	32.1	51.8	65.1	17.3	8.6	64.7
4	30.8	56.6	72.5	19.4	8.9	67.6
5	33.0	53.0	65.8	17.4	9.1	61.9

(g) Polymer L

Oleic Acid Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	34.2	61.0	74.3	19.6	10.9	74.4
0.5	36.2	34.6	40.9	10.7	6.6	51.4
1	36.7	32.4	38.0	9.9	6.3	50.1
2	30.9	54.6	70.0	18.6	8.7	69.5
4	33.8	48.4	59.3	15.7	8.5	56.8
5	39.6	32.6	36.5	9.4	6.9	49.3

Creosote Additions (kg/tonne)

(h) Polymer B

Creosote Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	32.5	55.0	68.8	18.2	9.3	63.2
0.5	34.9	61.4	74.0	19.5	11.2	64.8
1	34.0	59.6	72.8	19.4	10.6	66.2
2	34.6	59.6	72.2	19.0	10.8	65.0
4	36.2	58.4	69.0	18.1	11.1	61.2
5	35.6	60.4	72.0	18.9	11.3	62.5

(i) Polymer D

Creosote Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	33.7	56.0	68.8	18.2	9.8	62.7
0.5	34.4	55.0	66.8	18.9	10.6	64.4
1	34.8	62.0	74.9	19.7	11.3	66.8
2	34.8	60.4	72.9	19.2	11.0	67.1
4	38.2	56.0	64.1	16.7	11.3	61.9
5	36.0	57.8	68.5	17.9	11.0	61.5

(j) Polymer F

Creosote Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	33.6	49.0	60.3	15.9	8.6	60.3
0.5	33.9	55.8	68.3	18.0	9.9	62.4
1	34.8	57.6	69.5	18.3	10.5	63.6
2	35.2	56.6	67.9	17.9	10.4	61.0
4	36.9	58.8	67.8	17.7	11.3	59.0
5	36.6	56.0	65.7	17.2	10.8	59.9

(k) Polymer G

Creosote Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	33.2	52.2	64.6	17.1	9.0	59.4
0.5	39.9	64.0	71.2	18.4	13.6	59.9
1	32.8	50.0	62.2	16.5	8.5	59.7
2	39.5	64.6	72.4	19.7	13.6	62.3
4	37.3	44.0	51.1	13.3	8.7	53.6
5	37.8	45.6	52.5	13.7	9.1	53.5

(ℓ) Polymer I

Creosote Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	33.3	47.8	59.0	15.6	8.3	56.3
0.5	32.1	57.0	71.7	19.0	9.5	65.6
1	32.2	51.4	64.5	17.1	8.6	62.2
2	38.8	71.2	80.7	20.9	14.7	65.5
4	35.4	51.8	62.0	16.3	9.6	60.0
5	35.9	46.6	55.3	14.5	8.8	55.3

(m) Polymer L

Creosote Dosage	% Ash in Sediment	% Weight Yield	% Comb. Recovery	Wt. of Coal in Sediment	Wt. of Shale in Sediment	% Ash in Suspension
0	34.2	61.0	74.3	19.6	10.9	74.4
0.5	32.6	52.0	64.9	17.2	8.8	61.2
1	31.7	50.4	63.7	17.0	8.2	62.2
2	32.8	61.0	75.9	20.1	10.4	69.0
4	35.5	48.0	57.3	15.0	9.0	57.0
5	37.2	47.2	54.9	14.3	9.3	55.9